no action

GEORGIA INSTITUTE OF TECHNOLOGY
OFFICE OF RESEARCH ADMINISTRATION

RESEARCH PROJECT INITIATION

Date: August 11, 1975

Project Title: Survey of Coosa Basin for Organic Contaminants From Carpet Processing

Project No: E-27-630

Principal Investigator Dr. Wayne Tincher

Sponsor: Environmental Protection Division; Ga. Dept. of Natural Resources

Agreement Period: From 7/29/75 Until 8/31/76

Type Agreement: Contract dated 6/12/75

Amount: $28,121

Reports Required: Monthly Progress Reports

Sponsor Contact Person (s):

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Assigned to: Textile Engineering

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GEORGIA INSTITUTE OF TECHNOLOGY
OFFICE OF CONTRACT ADMINISTRATION

SPONSORED PROJECT TERMINATION

Date: 3/8/79

Project Title: Survey of Coosa Basin for Organic Contaminants from Carpet Processing

Project No: E-27-630

Project Director: Dr. Wayne C. Tincher

Sponsor: Georgia Department of Natural Resources; Environmental Protection Division; Atlanta, GA 30334

Effective Termination Date: January 31, 1979

Clearance of Accounting Charges: January 31, 1979

Grant/Contract Closeout Actions Remaining:

None

GRANTS & CONTRACTS ACCOUNTING: Please send OCA a copy of the final invoice on this project for our file.

_ Final Invoice and Closing Documents
_ Final Fiscal Report
_ Final Report of Inventions
_ Govt. Property Inventory & Related Certificate
_ Classified Material Certificate
_ Other _____

Assigned to: Textile Engineering (School/Laboratory)

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CA—4 (3/76)

E-27-630

Monthly Progress Report Number 1

August 1 - September 1, 1975

Survey of Coosa Basin for Organic Contaminants from Carpet Processing

Environmental Protection Division
Department of Natural Resources
State of Georgia

Prepared Under Contract No.
E-27-630

by

Wayne C. Tincher
School of Textile Engineering
Georgia Institute of Technology
Atlanta, Georgia 30332

I. Introduction

This report will be devoted to an assessment of the types of materials present in carpet processing effluents and to the current status of analytical techniques for these materials. The materials have been divided into 5 categories and each of these is discussed below.

II. Inorganic Compounds

Approximately 13 million pounds of inorganic compounds were discharged in 1974 by the carpet processing industry. Major components are:

Monosodium phosphate	Sodium hydroxide
Trisodium phosphate	Ammonium sulfate
Tetrasodium pyrophosphate	Diammonium hydrogen phosphate
Sodium carbonate	Ammonium acetate
Ammonium hydroxide	Sodium and zinc salts

Analytical techniques for these materials are, in general, readily available. Analysis for sulfur, phosphorous, sodium, and zinc should provide the necessary information on these materials. At least one dye used in large volume contains cobalt which should also be determined in carpet effluents.

III. Volatile Organics

A number of the organic components of textile wastes are sufficiently volatile to be determined by gas chromatography. Included in this group are:

Acetic acid	Naptha
Formic acid	2-ethyl hexanol
Biphenyl	Benzyl alcohol
Methyl benzoate	Mercaptobenzothiazole
Naphthalene	Diethyldithiocarbamate
Caprolactam	Mineral oil
Trimene	2,4-dimethyl-6-acetoxy-m-dioxane
Trichlorobenzene	Monochlorobenzene
Isopropyl alcohol	

Most of these compounds have already been detected in textile processing wastes. An estimated 40 million pounds of these materials were discharged in 1974.

IV. Dyes

This group contributed approximately 0.3 million pounds to carpet industry wastes in 1974. Over 50% of this total consisted of 12 dyes.

Disperse Yellow 23	Acid Red 151
Acid Yellow 19	Acid Red 337
Acid Yellow 151	Disperse Red 60
Acid Yellow 135	Acid Orange 128
Disperse Yellow 3	Disperse Blue 120
Disperse Yellow 57	Acid Blue 40

Analytical techniques for dyes in waste water are practically non-existant. In the previous work at Georgia Tech an analytical procedure has been developed that involves concentration of the dyes on a macroreticular resin column (XAD-2) followed by elution with methanol, benzene, and dimethylformamide. The eluents can be concentrated by evaporation of the solvent and spotted on silia gel thin-layer chromatograpy plates. Development with 75% $CHCl_3$-25% EtOH mixture gives good separation of the acid dye components and development with 25% dioxane-75% carbon tetrachloride gives good separation of disperse dyes as indicated in Figure 1. Quantities of each dye can be determined by removal of the spots from the plates, solution of the dye in a dimethyl formamide-water solution, and measurement of absorbance at selected wavelengths in the visible absorption spectrum. In cases where dyes of different colors are not completely resolved, the absorbance is measured at 2 or 3 wavelength and the quantities determined by solution of 2 or 3 simultaneous linear equations. Although somewhat cumbersome, this

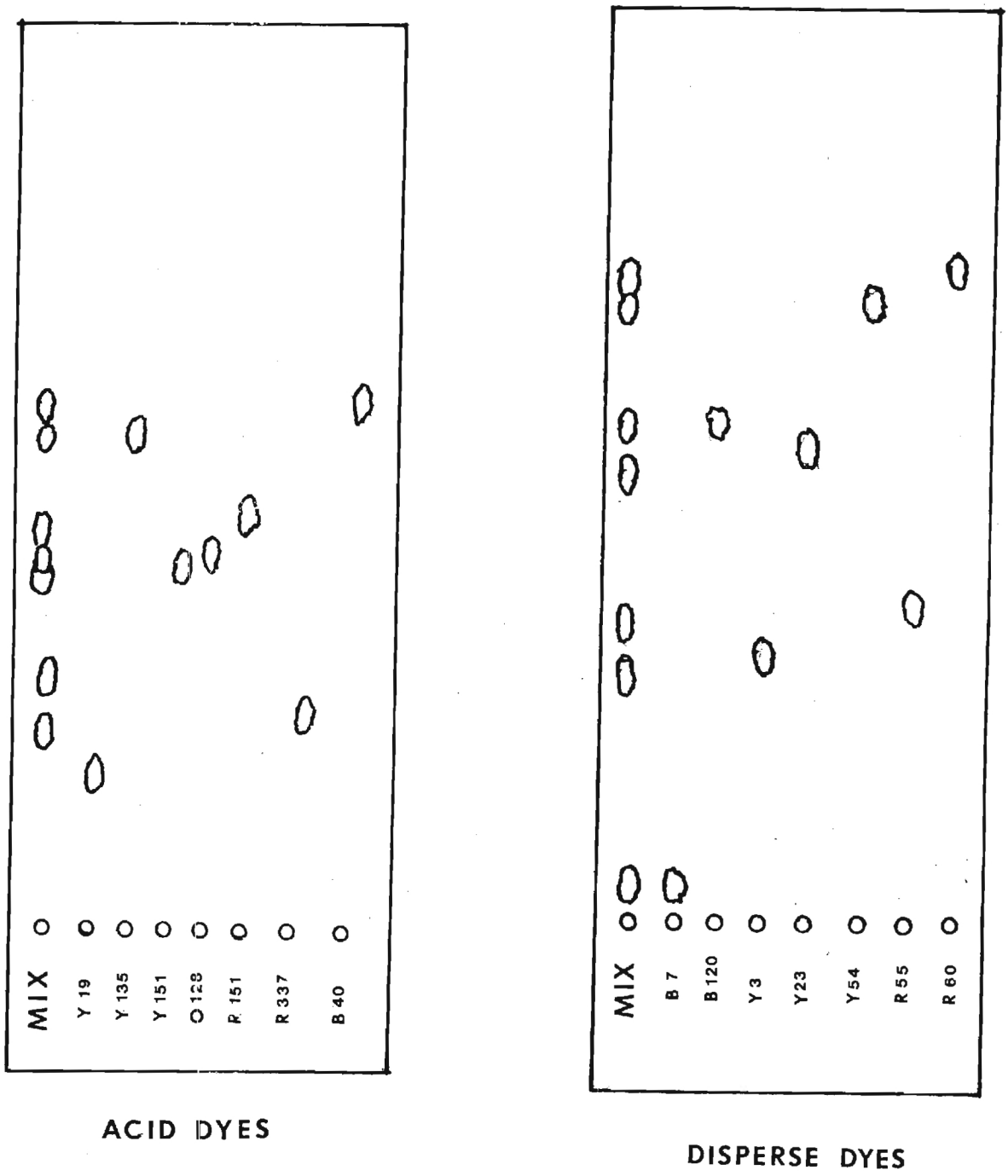

Figure 1 -- Separation of Acid and Disperse Dyes by Thin Layer Chromatography

procedure can be used to quantitate most of the important carpet dyes.

V. Surfactants

This large class of textile processing chemicals accounts for approximately 16 million pounds of carpet waste. The following types of compounds are used:

ethylene oxide adducts of fatty acids
ethylene oxide adducts of phenols (nonyl, octyl)
ethylene oxide adducts of fatty alcohols (C_{12} - C_{18})
ethylene oxide adducts of fatty amines (C_{12} - C_{18})
naphthalene sulphonate
sodium salts of sulphated alcohols
lignin sulphonate
quatenary ammonium salts of long chain hydrocarbon fatty acid amides

Analytical techniques are available for anionic surfactants as a group. These tests generally depend on development of color in solutions containing these surfactants and the intensity of color formation can be used for quantitation. Several color forming reagents are being investigated at the present time to determine the best technique.

Procedures are not available for nonionic surfactants. It has been recently discovered that ethylene oxide adducts of both octyl and nonyl phenol fluoresce when excited with radiation near 300 nm. Fluoresence has also been observed from naphthalene sulphonate and lignin sulphonate. This technique is now under investigation for possible quantitative analytical applications for there surfactants.

VI. Other Nonvolatile Organic Components

Several other organic components are present in carpet processing effluents. The principal materials are

polyester oligomers	1.5 million pounds
sequestrants	0.2 million pounds
gums	10.2 million pounds

Procedures are available for sequestrants but procedures are not available for the other two components in this group.

VII. Future Work

An assessment of the applicability of high pressure liquid chromatography to analysis of textile processing effluents and an evaluation of commercially available equipment will be reviewed next month.

E-27-630

Monthly Progress Report Number 2

September 1 - October 1, 1975

Survey of Coosa Basin for Organic Contaminants for Carpet Processing

Environmental Protection Division
Department of Natural Resources
State of Georgia

Prepared Under Contract No.
E-27-630

by

Wayne C. Tincher
School of Textile Engineering
Georgia Institute of Technology
Atlanta, Georgia 30332

I. Introduction

The Gas Chromatograph - Mass Spectrometer - Computer analysis system has proven very effective in separation, detection, and quantitation of trace organic components in water. Unfortunately a significant portion of the organic compounds in carpet mill wastes are not volatile. These species can be determined by GC-MS only with great difficulty if at all. Other techniques have therefore been sought to assist in analysis of carpet processing wastes.

A major effort this month has been directed toward assessing the possible applications of liquid chromatography to separation and analysis of non-volatile organic components in streams. The various instruments available have also been surveyed.

II. Applicability of Liquid Chromatography

Recent developments in technology have made rapid and quantitative separation of complex mixtures possible by high pressure liquid chromatography. In this technique, components to be separated are dissolved in a suitable solvent and pumped into a small column containing a small particle, high surface area adsorbant. The differing partition of the various components between the stationary phase and the moving solvent phase results in a separation of the components as they move down the column. The instrument may be operated in a variety of modes depending on the nature of the stationary phase. In the case of small particle silica columns, a type of adsorption chromatography is responsible for the separation. In other cases a liquid-like hydrocarbon (e.g. C_{18} chains) are absorbed on or bonded to the column and a type of liquid-liquid partition is achieved. In other cases ionic species are bonded to the column for separation of polar components. Columns containing

specific pore sizes are also available to obtain separations based on molecular size (exclusion chromatography). This range in operation mode combined with the variety of solvents and solvent mixtures which may be used as mobile phases provides an extremely versatile separation tool.

Detection of components exiting from the column is usually achieved by absorption in the UV and/or visible spectrum. Thus, the detector systems are especially sensitive to dye molecules and the aromatic portions of many surfactant molecules. Other detectors are available (fluorescence, refractive index) and can be used in series with up to 4 detectors operating simultaneously.

III. Proposed Analytical Procedure

The scheme which we plan to use initially for analysis of carpet waste samples will involve 3 basic steps - concentration, separation, and quantitation. Concentration will be achieved by passing 20 liters or more of water containing dye waste through a column containing XAD-2 resin. The column will be back-washed with small portions of methanol, benzene, and dimethylformamide to remove dyes and other organic components. The column extracts will be evaporated to dryness and the organic components dissolved in a solvent suitable for injection in the liquid chromatography unit for separation.

For dye molecules, the UV-visible detector in the chromatographic unit can be used directly for quantitation. The combination of retention time and position of UV absorption peak should be an adequate means of identification. Retention times and fluorescence excitation and emission peaks will be used for aromatic surfactant identification and quantitation.

There is the possibility that for dye analyses liquid chromatography

alone may be used. In this scheme dye would be concentrated by passing the appropriate quantity of water through a silica column containing a bonded C_{18} hydrocarbon chain on the surface to concentrate the dye on the column. This concentration step would be followed by elution of the dye in an organic solvent and passage directly to a separation column of silica gel. The retention time and UV absorption peak would be used for identification and quantitation. The feasibility of this procedure is being investigated by one instrument manufacturer with 15 selected carpet dyes we supplied to him.

IV. Instrument selection

A careful comparison of the specifications of the leading liquid chromatography instruments has been made. The instruments most suited to waste analysis would appear to be those manufactured by Micrometrics or Waters Associates.

V. Future Work

Analytical methods for quantititive analyses for surfactants will be reviewed next month.

Monthly Progress Report Number 3

October 1 - November 1, 1975

Survey of Coosa Basin for Organic Contaminants for Carpet Processing

Environmental Protection Division
Department of Natural Resources
State of Georgia

Prepared Under Contract No.
E-27-630

by

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Atlanta, Georgia 30332

I. Introduction

Major effort this month has been directed toward further development of quantitative tests for surfactants and to preparation for high pressure liquid chromatographic experiments on separation of disperse dyes.

II. Analyses for Surfactants

A number of colorimetric tests are reported in the literature for confirming the presence of surfactants and identifying the charge type (anionic, cationic, nonionic, ampholytic). These tests are based either on the ability of small quantities of surfactants to solubilize normally water-insoluble dyes or on formation of water-insoluble colored salt complexes between dyes and surfactants.

One of these tests (formation of colored salts with Thymol blue) has been investigated for quantitation of anionic and cationic surfactants. Results suggest that this procedure is not sensitive enough for surfactants in textile wastes.

A modification of this procedure may have promise for anionic surfactants. Fluoresceine forms a fluorescent compound with anionic surfactants which may be useful in quantitative analyses. This possibility will be investigated.

All materials have been ordered and received to study the applicability of the Dragendorff test for nonionic surfactants and the triphenyl tetrazolium chloride test for anionic surfactants. These procedures will be evaluated in the near future.

III. Preparation of Standard Dye Solution

Well characterized dye solutions will be required for the proposed liquid chromatography experiments. Seven disperse dyes have been selected for the initial work

Disperse Blue 7

Disperse Red 60

Disperse Red 55

Disperse Blue 120

Disperse Yellow 23

Disperse Yellow 54

Disperse Yellow 3

Five to ten gram samples of highly purified dyes were prepared by placing the commercial dye in a soxhlet thimble and extracting with benzene for 24 hours. The benzene soluble dye was recovered in a Rotovap unit and the pure dye dried prior to preparation of standard solutions.

Previous studies had indicated that difficulties would be encountered in attempting to dissolve some purified dyes in benzene. Experiments suggested that if the dyes were first pasted with a small quantity of dimethylformamide, complete solution in benzene is possible. This procedure was used in preparation of the standard dye solutions.

Ten milligrams of each dye was weighed on a six place analytical balance and pasted with 1 ml of dimethylformamide in a small beaker. The dye solution was rinsed into a 100 ml volumetric flask with

benzene and after repeated rising with benzene the solution was diluted to the mark giving 100 ml of a 100 ppm purified dye solution. These solutions will be used for liquid chromatography studies and to prepare UV-visible absorption spectra of the pure dyes. Curves of absorbance versus concentration of the pure dyes in DMF-Benzene 1:99 solutions will be prepared.

IV. Future Work

Further work in preparation for the liquid chromatography experiments will be reported next month.

Monthly Progress Report Number 4

November 1 - December 1, 1975

Survey of Coosa Basin for Organic Contaminants from Carpet Processing

Environmental Protection Division
Department of Natural Resources
State of Georgia

Prepared Under Contract No.
E-27-630

by

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I. Introduction

Preparations for high pressure liquid chromatography studies on disperse dyes have continued this month. Fluorescence spectra of a number of aromatic type surfactants have also been investigated in greater detail.

II. Preparation for Liquid Chromatography Studies

A high pressure liquid chromatograph suitable for separation and quantitation of dyes in waste water has been located and arrangements completed to initiate studies on disperse dyes. The instrument is a Micromeritics Model 7000 equipped with a variable wavelength UV-visible detector and with capabilities for both isocratic and gradient operation. Two columns have been suggested for initial studies--a small particle (10μ) silica column and a silica column modified by reaction to incorporate nitrile groups on the column (Partisil PAC). These columns will separate dyes on the basis of differences in polarity.

Solubility studies on disperse dyes have been carried out to assist in selection of the mobile phase for liquid chromatography experiments. The following polar solvents--tetrahydrofuran, isopropyl alcohol, methyl alcohol, dimethylformamide--appear to dissolve disperse dyes sufficiently to serve as the strong solvent. Isooctane, cyclohexane, and heptane will be tried as weak solvents.

Absorption spectra of dyes have been investigated to select optimum settings for the UV-visible detector. Typical absorption curves for red, yellow and blue disperse dyes are shown in the attached figures.

It is apparant from these curves that different detector wavelength settings will be required for the red, yellow and blue dyes. A complete analysis will probably require three runs with the detector set at 420, 520, and 620 nanometers.

Standard dye solutions have been prepared and all solvents have been ordered to begin liquid chromatography studies next month.

III. Fluorescence Spectra of Aromatic Surfactants

Fluroescence spectra of several representative aromatic surfactants used in carpet processing have been obtained. Tamol SN (100 ppmin H_2O) is a typical naphlthalene sulfonate used as a leveling agent and disperant. The fluorescence is excited at 350 nm with emission at 290 nm. The fluorescence intensity is quite high and surfactants of this type can probably be determined at 1 ppm or below. Igepal CA-620, a typical ethylene oxide adduct of nonyl phenol, emits at 300 nm with excitation at 420 nm. The fluorescence emission is not as intense as Tamol SN, but 1 ppm in solution can probably be detected. Reax 85 A, a typical lignin sulfonate absorbs at 330 nm and 420 nm. The fluorescence is much weaker than the other two aromatic surfactants.

IV. Future Work

Initial high pressure liquid chromatography experiments and preparation of analytical working curves for fluorescent surfactants is planned for next month.

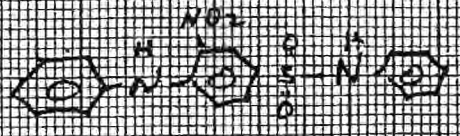
GENERAL ELECTRIC RECORDING SPECTROPHOTOMETER

X =
Y =
Z =

x =
y =

Disperse Yellow 42
Cell conc. 0.36456 g/1
Solvent: DMAC//20/80

X	83.1	x	0.374
Y	93.7	y	0.422
Z	45.5		



100
90
80
70
60
50
40
30
20
10
0

380 400 20 40 60 80 500 20 40 60 80 600 20 40 60 80 700

BY

TEST NO. 6

INST. NO. 4244135

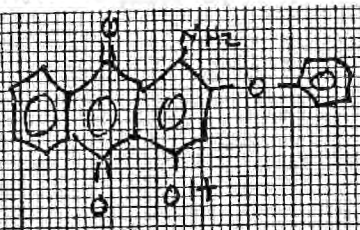
C227K30001

GENERAL ELECTRIC RECORDING SPECTROPHOTOMETER

X=
Y=
Z=

Disperse Red 60
Cell conc. 0.13726 g/l
Solvent: DMAC//20/80

X	69.1	x	0.382
Y	44.9	y	0.248
Z	67.1		



STD.

PERCENT TRANSMITTANCE REFLECTANCE

100
90
80
70
60
50
40
30
20
10
0

380 400 20 40 60 80 500 20 40 60 80 600 20 40 60 8

GENERAL ELECTRIC RECORDING SPECTROPHOTOMETER 5

PERCENT TRANSMITTANCE REFLECTANCE

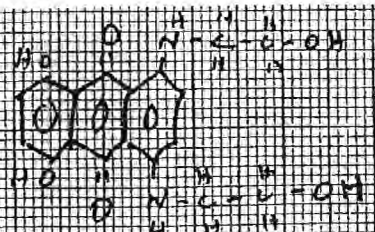
100
90
80
70
60
50
40
30
20
10
0

X1=
Y1=
Z1=

X1=
Y1=

Disperse Blue 7
Cell conc. 0.08770 g/1
Solvent: DMAC//20/80

X	45.6	x	0.224
Y	56.0	y	0.274
Z	102.4		



3/9/72

BY

TEST NO 10

4244135

380 400 20 40 60 80 500 20 40 60 80 600 20 40 60 80 700

MILLIMICRONS

Monthly Progress Report Number 5

December 1 - January 1, 1976

Survey of Coosa Basin for Organic Contaminants from Carpet Processing

Environmental Protection Division
Department of Natural Resources
State of Georgia

Prepared Under Contract No.
E-27-630

by

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I. Introduction

Major effort this month has been devoted to development of high pressure liquid chromatography techniques for determination of disperse dyes in waste water. The six dyes selected for initial study include Disperse Yellow 54, Disperse Yellow 3, Disperse Yellow 23, Disperse Red 55, Disperse Red 60, Disperse Blue 120, and Disperse Blue 7. These dyes are used in large quantities in beck dyeing of carpet.

II. Liquid Chromatography Studies

Standard solutions containing 100 ppm and 10 ppm of each of the disperse dyes listed about were prepared for initial high pressure liquid chromatography studies. In addition a mixture containing 10 ppm of each of the dyes was also prepared. These solutions were prepared in a solvent mixture containing 99% benzene and 1% dimethylformamide.

Based on previous thin layer chromatography work, it was expected that a small particle (10μ) silica column would be the column of choice for achieving separation of these dyes. A column of this type was installed in the Micromerities Model 7000 high pressure liquid chromatography instrument Dyes that had eluted rapidly and slowly in the thin layer chromatography experiments were selected to check the column selection. Eight microliters of a 100 ppm solution of Disperse Blue 7 was injected on the column and developed with a solvent mixture containing 75% carbon tetrachloride and 25% dioxane. Disperse Blue 7 was so strongly absorbed on the column that it could not be removed with this solvent mixture.

A number of other solvents were then investigated and it was discovered that the small particle silica column adsorbed dyes so strongly that good separations could not be achieved. Subsequent experiments with a column containing long chain hydrocarbon groups (C-18) bonded to the column were attempted next. Dyes were very poorly adsorbed on this column and good separations were not obtained.

Discussion of the separation problem with several chromatographic equipment manufacturers led to the selection of a silica column with cyanoethyl groups chemically bonded to the silica for separation of disperse dyes. This column is intermediate in polarity (compared to Carbon-18 bonded columns and silica columns) and was felt to be the best available choice for organic compounds with structures of the disperse dye type. A solvent system consisting of a nonpolar major component (nonsolvent) and a polar component (solvent) were suggested for elution of the dyes. Preliminary experiments were conducted with a number of nonsolvents (isooctane, carbon tetrachloride, hexane, cyclohexane, benzene)and solvents(dioxane, dimethylformamide, tetrahydrofuran). These experiments suggest that the cyanoethyl bonded column is of the right polarity for disperse dye separations. Further work will be required to select the best solvent system.

III. Future Work

Effort next month will be directed to selection of the best solvent system for separation of disperse dyes.

Monthly Progress Report Number 6

January 1 - February 1, 1976

Survey of Coosa Basin for Organic Contaminants from Carpet Processing

Environmental Protection Division
Department of Natural Resources
State of Georgia

Prepared Under Contract No.
E-27-630

by

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School of Textile Engineering
Georgia Institute of Technology
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I. Introduction

Effort this month has been directed toward selection of a solvent system for separation of disperse dyes by high pressure liquid chromatography.

II. Liquid Chromatography Studies

Separation of the following seven disperse dyes

Disperse Blue 120

Disperse Blue 7

Disperse Red 55

Disperse Red 60

Disperse Yellow 54

Disperse Yellow 42

Disperse Yellow 3

is being investigated using a cyanoethyl bonded silica liquid chromatography column. This column gave best separation of disperse dyes in preliminary studies reported last month. Selection of a mixture of a nonpolar nonsolvent and a polar solvent for optimum separation of the dye mixture has received major attention this month.

Dipserse Blue 7 is very strongly adsorbed on the cyanoethyl bonded column (Pastisil PAC Column by Reeve Angel). This dye was selected, therefore, for screening studies on solvent systems. The solvent or mobile phase must be capable of eluting the strongest held solute from the column in a reasonable time. Disperse Blue 7 served on a effective test sample for solvent screening.

The following solvent - nonsolvent systems in various combination were investigated for elution of Disperse Blue 7

Nonsolvent	Solvent
isooctane	dioxane
carbon tetrachloride	dimethylformamide
hexane	tetrahydrofuran
cyclohexane	dimethylacetamide
benzene	

Although a number of pairs of these solvents would elute Disperse Blue 7 considerations of solvent purity and cost led to selection of cyclohexane as the nonsolvent and tetrahydrofuran as the solvent.

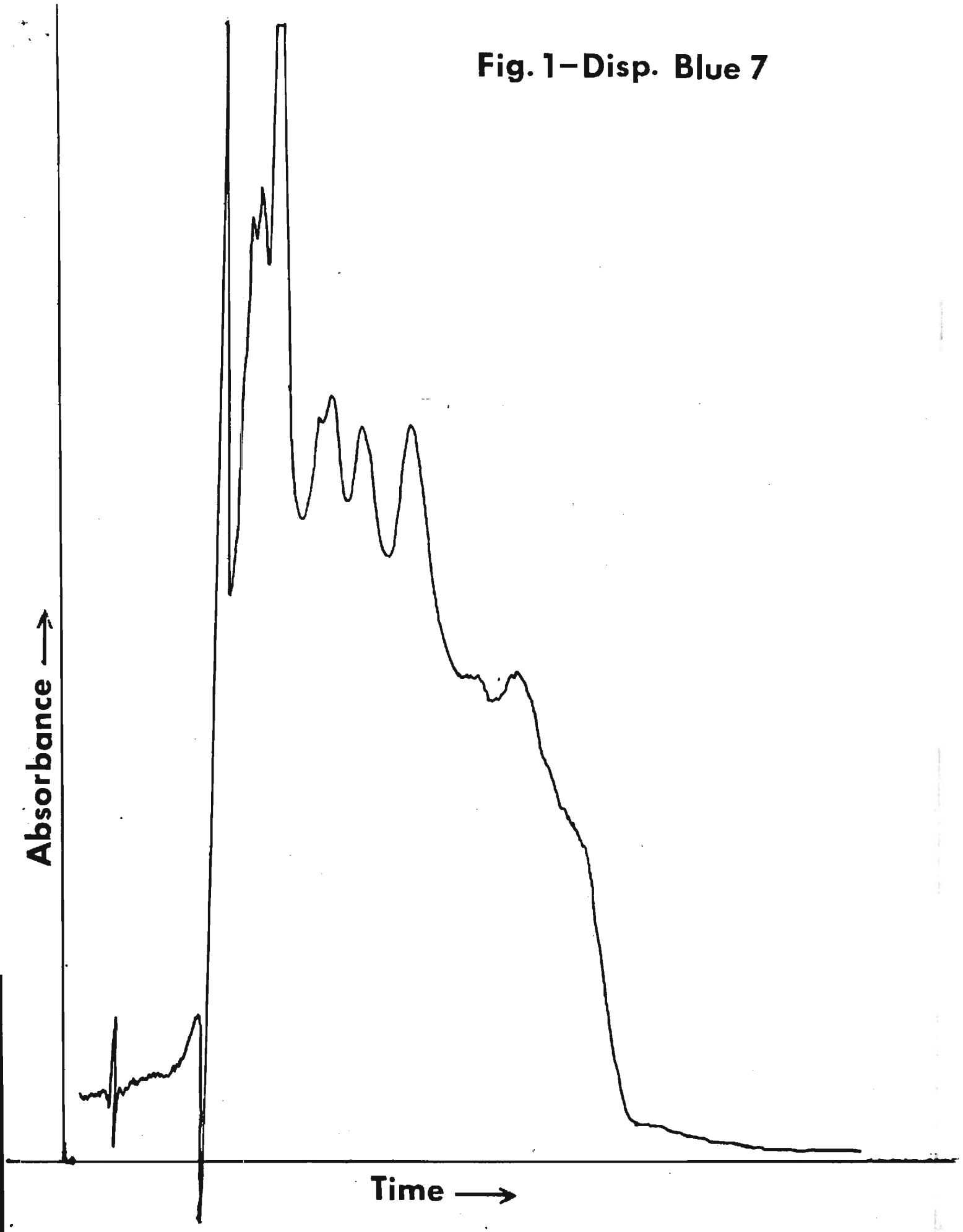
During the course of these experiments an interesting chromatograph of Disperse Blue 7 was obtained and is shown in Figure 1. The dye used in preparation of the standard solution of Disperse Blue 7 had been separated from the dispersing agents by solvent extraction. Despite this purification, the dye consists of at least 10 components as shown by the chromatogram (Mobile phase - 81.25% tetrahydrofuran, 18.25% cyclohexane; detector 629 nm; flow 2 ml/minute). Most of these components are probably reaction products inherent in the dye manufacturing process. The ability to separate these very similar components demonstrates the capabilities of the liquid chromatography technique.

Increasing the nonsolvent component in the mobile phase reduces the separation of the various components and inhances the sensitivity of the technique for the Disperse Blue 7 dye mixture.

III. Future Work

Experiments with the cyclohexane - THF mobile phase with other disperse dyes will be carried out next month. Attendance at a high pressure liquid chromatography symposium and presentation of a review of the research project for Environmental Protection Division personnel are planned next month also.

Fig. 1–Disp. Blue 7



Monthly Progress Report Number 7

February 1 - March 1, 1976

Survey of Coosa Basin for Organic Contaminants from Carpet Processing

Environmental Protection Division
Department of Natural Resources
State of Georgia

Prepared Under Contract No.
E-27-630

by

Wayne C. Tincher
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Atlanta, Georgia 30332

I. Introduction

Major effort his month has been directed toward collecting data on retention volumes for disperse dyes on a Partisil PAC column with a cyclohexane - tetrahydrofuran mobile phase.

II. Liquid Chromatography Studies on Disperse Dyes

The purified seven disperse dyes (blue 7, blue 120, red 60, red 55, yellow 23, yellow 54, and yellow 3) dissolved in 99% benzene 1% dimethylformamide were injected one at a time in the Micromeritics Liquid Chromatography and eluted isocratically with various mixtures of cyclohexane and tetrahydrofuran. Elution volumes for different ratios of solvent and non-solvent are shown in Table 1. There is some scatter in the data due to the fact that the solvent mixing valve was not functioning properly during some of the runs. However, the data do permit several conclusions essential to selection of a solvent system for the mobile phase.

First it appears that the best separation will be achieved by gradient operation rather than isocratic operation. The faster moving dyes are too near the solvent front with high concentrations of the strong solvent (THF) and the slower moving dyes are on the column too long with lower concentrations of strong solvent.

Second, the data suggest that a beginning strong-to-weak solvent ratio of about 25 to 75 will separate the solvent front from the fast moving dyes and that 100% strong solvent gives adequate removal of the slowest moving dye (DB7). A gradient beginning at 25/75 and increasing linearly to 100% strong solvent will be investigated.

III. Other Project Related Activities

A two day symposium on liquid chromatography equipment and techniques was attended on February 10 and 11. This symposium was very helpful in elucidating various problems in liquid chromatography and in suggesting experimental procedures for good separation.

A review of the two projects conducted at Georgia Tech under sponsorship of EPD was presented to EPD personnel on February 9.

Table 1

Elution Volumes (ml) for Disperse Dyes on Partisil PAC
with Cyclohexane - THF mobile phase (Isocratically)

Dye	25/75	30/70	35/65	40/60	50/50	60/40	75/25	80/20	81/19	90/10
DB 120	7.0	8.8	4.9	6.4	3.8		3.5			
DR 60	5.1		4.3		3.6	4.3				
DY 54	6.1		4.9		3.9					
DY 23	10.2		7.8		4.8				3.4	
DB 7								14.9		10.9
DR 55				4.0	9.4	5.2				
DY 3					15.7			3.6	4.9	

Monthly Progress Report Number 8

March 1 - April 1, 1976

Survey of Coosa Basin for Organic Contaminants from Carpet Processing

Environmental Protection Division
Department of Natural Resources
State of Georgia

Prepared Under Contract No.
E-27-630

by

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I. Introduction

Due to problems with the Micromeritics Liquid Chromotography Instrument, development of separation and quantitation of disperse dyes has been delayed. Major effort this month has therefore been directed toward defining column configuration and procedures for concentration of disperse dyes. A procedure has been developed which is compatible with the liquid chromotograph and which gives good recovery of the dyes from waste water.

II. Dye Concentration Procedures

Studies reported earlier have indicated that macroreticular resins can effectively remove dyes from waste water and that the adsorbed dyes may be removed from the column with selected solvents such as benzene, methanol, and dimethylformamide. By running a large volume of waste water through the column and backwashing with a small volume of solvent, a substantial increase in concentration can be achieved.

A number of experimental parameters have been studied to establish details of the concentration procedure. In these studies, 1 ppm solutions have been passed through resin columns and the amount of the dye present which is recovered was determined. The effect of column diameter was investigated by using both 1 cm and 2 cm columns. The results indicated that column diameter did not influence the recovery. Subsequent studies were therefore carried out on the smaller columns so that smaller overall volumes of waste and recovery solvents could be used.

Resin bed depths of approximately 25 and 40 cm were investigated in a further attempt to reduce the scale of the experiments. Recoveries were slightly better at 40 cm so the longer columns will be used in all subsequent work.

The concentration procedure that is now being used is as follows. A resin column is prepared by slurrying XAD-2 resin beads in methanol. A 1 cm X 50 cm resin column is filled with the slurry and the methanol allowed to flow from the bottom of the column. This procedure is continued until approximately 40 cm of resin has been added to the column. The column is then backwashed with methanol to remove fines. The top of the column is plugged with glass wool and then washed with water to replace the methanol. The column is then ready for concentration of waste.

In recovery studies, 200 ml of a 1 ppm dye solution in 10% DMF and 90% water were passed through the column at 8 bed volumes per hour (approximately 350 ml/hour). The column was then washed with 50 ml of 10% DMF-water, inverted and the disperse dyes removed by backwashing with 40 ml of benzene. The acid dyes are next removed by backwashing first with 80 ml of dimethyl-formamide and then 40 ml of methanol. The disperse dyes were dried in a Rotavap unit and the dye taken up in 20 ml of a 1% dimethylformamide 99% benzene solvent. The acid dyes were treated similarly except they were taken up in a 1% dimentylformamide, 99% methanol solvent. These solutions are now ready for injection in the Micrometrics liquid chromatograph for separation and quantitation.

Recovery of disperse dyes by this procedure is shown in Table 1. The current studies agree quite well with the more limited data previously collected and demonstrate the effeciency of the concentration procedure. Similar data are now being collected for acid dyes.

III. Future Work

The liquid chromatograph has been repaired and studies will be continued

next month on separation and quantitation of disperse dyes.

Table 1

Recovery of Disperse Dyes

	Current	Previous
Disperse Red 60	66%	93%
Disperse Blue 120	83%	-
Disperse Red 55	95%	85%
Disperse Blue 7	73%	-
Disperse Yellow 54	77%	-
Disperse Yellow 3	98%	99%
Disperse Yellow 23	77%	84%

Monthly Progress Report Number 9

April 1 - May 1, 1976

Survey of Coosa Basin for Organic Contaminants from Carpet Processing

Environmental Protection Division
Department of Natural Resources
State of Georgia

Prepared Under Contract No.
E-27-630

by

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I. Introduction

Efforts to develop a satisfactory separation and quantitation scheme for disperse dyes continued this month following repair of the Micromerities High Pressure Liquid Chromatograph.

II. Separation and Quantitation of Disperse Dyes

Experimental conditions have been established which give good separation of disperse dyes by liquid chromatography. Eight microliter samples of the dyes (10 ppm) dissolved in 99% benzene 1% dimethylformamide were injected in the liquid chromatograph equipped with a Partisil PAC Column (Reeve Angle). The samples were eluted with a solvent mixture of cyclohexane and tetrahydrofuran. The initial solvent concentration was 25/75 (v/v) tetrahydrofuran/cyclohexane with the tetrahydrofuran concentration increased linearly during the run to 100%. A flow rate of 1 ml/min was used and the variable wavelength uv/visible detector set at a wavelength appropriate for the color of the dyes being separated.

A typical curve for the yellow dyes is shown in Figure 1. In this case the detector was set at 420 nm which is near the peak absorption for yellow dyes. Disperse yellow 54, disperse yellow 23 and disperse yellow 3 are clearly separated by this procedure. Similar separations have been achieved for the disperse red dyes (detector set at 520 nm) and the blue disperse dyes (detector set at 620 nm).

Preliminary results suggest that the dyes can be quantitated directly from the photocell output by integration of the areas under the liquid chromatograph peaks.

III. Future Work

Development of analytical working curves for quantitation of dyes in mixtures will be attempted next month.


SOLVENT
DY 3
DY 54
DY 23
ABS
TIME

Monthly Progress Report Number 10

May 1 - June 1, 1976

Survey of Coosa Basin for Organic Contaminants from Carpet Processing

Environmental Protection Division
Department of Natural Resources
State of Georgia

Prepared Under Contract No.
E-27-630

by

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I. Introduction

Work has continued this month on development of an analytical system for disperse dyes in waste water. A suitable system for disperse yellow dyes has been developed and is described below.

II. Liquid Chromatography Studies on Disperse Dyes

As reported last month, experimental conditions have been established which give good separations of disperse dyes by high pressure liquid chromatography. The techniques described last month have been used to develop analytical working curves which will permit both separation and quantitation of the disperse dyes in mixtures.

Typical liquid chromatograms of 20, 10 and 5 ppm solutions of disperse yellow 54 are shown in Figure 1. The absorbance of the eluent at 420 nm is shown as a function of the volume of the elution solvent. The sharp pressure change at injection can be clearly seen at the left of the chromatogram followed by a series of peaks due to the solvent used (benzene/DMF at 99/1) for the dye as it leaves the column. Although the solvent does not absorb at 420 nm, the refractive index change as the solvent passes through the detector gives the characteristic peak structure identified as the solvent front. The absorption peak for disperse yellow 54 is well resolved to the right of the solvent front. As indicated last month, this peak is also well separated from the other two disperse yellow dyes (23 and 3) of interest in this study.

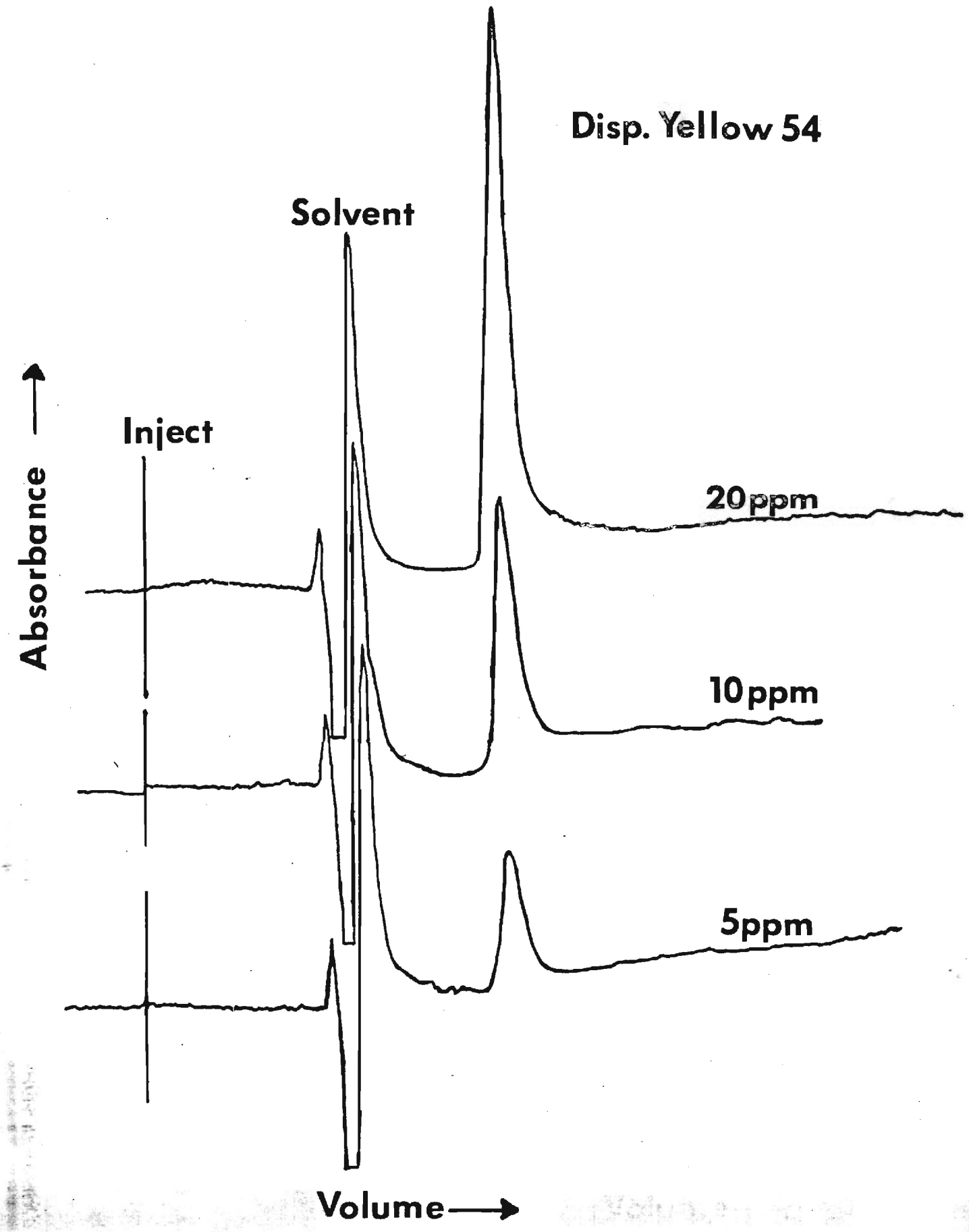
The peaks from the disperse yellow 54 spectra were cut out and weighed

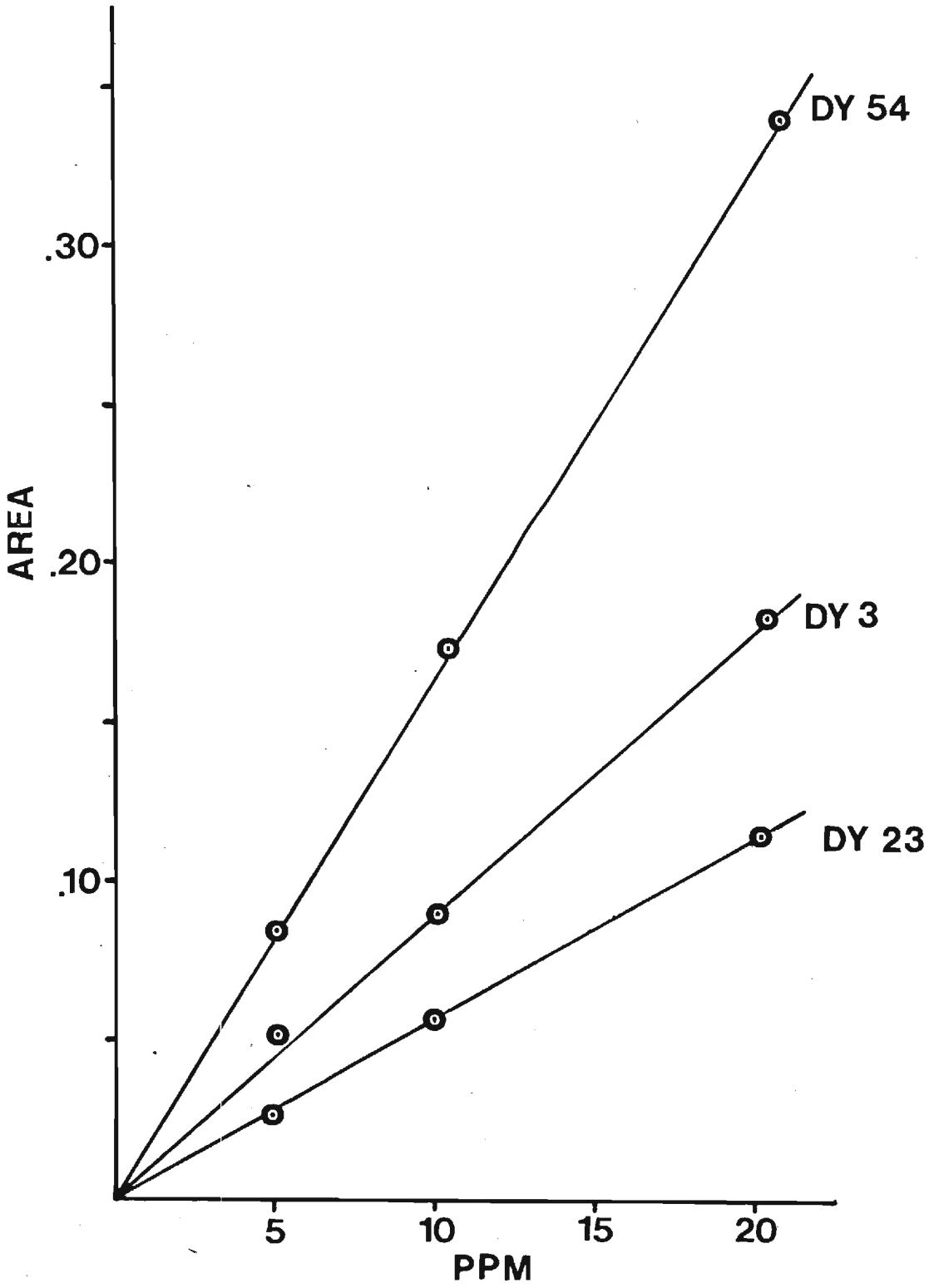
On an analytical balance to obtain relative areas under the curves. The relative areas are shown in Figure 2 plotted versus the concentration of dye in the injected sample in parts-per-million (ppm). Similar curves for disperse yellow 23 and disperse yellow 3 are also shown in Figure 2.

These results suggest that it should be possible to determine the disperse yellow dyes in waste water quantitatively at less than 1 ppm with a ten-fold concentration step (resin column absorption) and separation and quantitation by liquid chromatography.

III. Future Work

Similar studies on blue and red disperse dyes and further work on recovery of acid dyes from waste water are planned for next month.


Disp. Yellow 54
Solvent
Inject
Absorbance
20ppm
10ppm
5ppm
Volume


DY 54
DY 3
DY 23
.30
.20
.10
AREA
5
10
15
20
PPM

Monthly Progress Report Number 11

June 1 - July 1, 1976

Survey of Coosa Basin for Organic Contaminants from Carpet Processing

Environmental Protection Division
Department of Natural Resources
State of Georgia

Prepared Under Contract No.
E-27-630

by

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I. Introduction

Primary effort this month has been directed toward development of analytical procedures for acid dyes in waste water. These dyes are characterized by the presence of ionizable groups in the dye structure. The dyes usually contain one or more sulfonic acid groups present as the sodium salt.

II. Recovery of Acid Dyes from Waste Water

Preliminary studies on some acid dyes ("Analysis for Organic Contaminants from Carpet Processing" Final Report, Project E-27-626, Part II) suggested that these dyes could be concentrated by passing solutions of the dye through macroretricular resins and back-washing the column with selected organic solvents. This procedure has been investigated in detail this month for the series of acid dyes shown in Table 1.

In these studies, 1 ppm solutions of the dyes in water containing a few percent dimethylformamide were passed through a column containing XAD-2 resins, a flow rate of approximately 4 bed volumes per hour (200 ml.) was maintained. The adsorbed dye was then removed from the column by back-washing with methanol. The quantity of dye in the eluent was determined with a Beckman DB-G spectrophotometer by comparison of the absorbance of the methanol solutions with absorbance of solutions of known concentration.

Results for the principal acid dyes used for carpet dyeing are shown in Table 1. Recoveries for Acid Yellow 151, Acid Red 337, Acid

Yellow 135 and Acid Blue 25 are acceptable but recovery of Acid Yellow 19, Acid Red 151 and Acid Orange 128 are lower than expected.

Reasons for this lower recovery are now under investigation. Due to the polar nature of these dyes, a slightly more polar resin may be necessary to achieve adequate removal from the waste water. If removal from the column is the source of the problem, a stronger solvent will be selected.

III. Analyses for Surfactants

All materials required for analyses of anionic surfactants (by the methylene blue active substances) and for nonionic surfactants have been received and development of standard working curves is underway.

IV. Future Work

A continuation of studies on recovery of acid dyes and procedures for separation of acid dyes by liquid chromatography will be reported next month.

TABLE 1

Recovery of Acid Dyes from Waste Water

Dye	λmax(nm)	% Recovery
Acid Yellow 19	418	30
Acid Yellow 151	440	75
Acid Yellow 135	400	100
Acid Red 151	510	40
Acid Red 337	509	75
Acid Orange 128	414	40
Acid Blue 40	623	57
Acid Blue 25	625	80

Monthly Progress Report Number 12

July 1 - August 1, 1976

Survey of Coosa Basin for Organic Contaminants from Carpet Processing

Environmental Protection Division
Department of Natural Resources
State of Georgia

Prepared Under Contract No.
E-27-630

by

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I. Introduction

Major effort this month has been devoted to development of methods for concentration of and analysis for acid dyes in waste water.

II. Concentration of Acid Dyes

As reported last month, three acid dyes (Acid Red 151, Acid Orange 128 and Acid Yellow 19) have presented difficulties in the concentration phase in that less than 50% of the dye present in known solutions could be recovered. Subsequent experiments have shown that the dye is quantitatively removed from the waste water by XAD-2 macroreticular resin and that the difficulty encountered is the removal of the dye from the column.

A number of approaches have been investigated to improve the recovery of these acid dyes from the column. The following series of complex equilibria are present for acid dyes:

$$\begin{array}{ccc} \text{dye} - SO_3H & \underset{Na^+}{\overset{H^+}{\rightleftharpoons}} & \text{dye}-SO_3Na \\ \downarrow\uparrow & & \downarrow\uparrow \\ \text{dye}-SO_3^- + H^+ & & \text{dye}-SO_3^- + N_a^+ \end{array}$$

Acid dyes are usually sold in the sodium salt form. The salt form readily ionizes in strongly polar solvents yielding soluble ion pairs. The acid form of the dye does not ionize as readily. Therefore in less polar solvents (most organic solvents) the acid form is more soluble. Two approaches were taken to increase the removal of acid dyes from the column. First, the adsorbed dye was eluted with methanol

followed by a 1% solution of ammonium hydroxide. An appreciable quantity of dye was removed in the ammonium hydroxide solution but recovery was still unacceptable with all of the acid dyes. The second procedure attempted involved first treating the absorbed dye with 1% formic acid to produce the less readily ionized form followed by elution with tetrahydrofuran. Although quantitative data are not yet available, this procedure appears to give good removal of the acid dyes from the column.

III. Separation of Acid Dyes by Liquid Chromatography

Considerable effort has been devoted this month to try to select the best possible system for use in separation of acid dyes by liquid chromatography. Since these dyes have one or more ionizable groups, an ion exchange column with pH of the eluting solvent as the separation parameter would appear to be the system of choice. However, discussion of ion exchange techniques with a number of people experienced in these types of separations suggested that reproducibility is poor and separations are difficult.

After survey of the possibilities, a new technique known as paired-ion chromatography has been selected for study. In this technique the dyes are adsorbed from a solution on a silica column containing C_{18} hydrocarbon groups bonded to the column. The dyes are eluted with methanol-water mixtures containing tetrabutylammonium phosphate. This technique has been used [Whittman, D.P., Nuessle, N.O., and Haney, W.G., Anal. Chem. 47, 1422(1975)] to separate food dyes very similar is structure to dyes of interest in the present study. All materials necessary to conduct paired-ion chromatography studies on acid dyes have been ordered.

IV. Future Work

Work on analysis for surfactants will be reported next month. Also, initial experiments on influent and effluent from the Dalton waste treatment facility will be carried out next month.

Monthly Progress Report Number 13
August 1 - September 1, 1976

Survey of Coosa Basin for Organic Contaminants from Carpet Processing

Environmental Protection Division
Department of Natural Resources
State of Georgia

Prepared Under Contract No.
E-27-630

by

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I. Introduction

Major effort this month has been directed toward continued development of the analytical system for disperse dyes. A suitable system for disperse red dyes has been developed and is described below.

II. Liquid Chromatography Studies on Disperse Red Dyes

Disperse Red 60 and Disperse Red 55 are among commonly used disperse dyes in carpet processing. Previous studies with these dyes have shown that they can be separated by liquid chromatography on a Partisil PAC column with a mixture of tetrahydrofuran and benzene as the elution solvent. Disperse Red 55 is bound more tightly to the column and does not elute until a very polar solvent mixture is used. Disperse Red 60 elutes quickly and most often appears very near the solvent front. The great disparity in elution times has created some problems in developing an analytical system for these dyes. The long elution time for disperse red 55 causes considerable spreading of the peak (probably due to multiple components in the dye) and a lower sensitivity than desired.

This problem has been overcome by elution of the disperse red dyes with two different solvent mixtures rather than the use of solvent gradients. The dye sample is injected on the column and eluted with a 35/65 mixture of tetrohydrofuran/benzene. The detector is set at 520 nm and the Disperse Red 60 peak appears just after the solvent front. A second sample is injected and eluted with an 80/20 mixture of tetrahydrofuran/benzene. The Disperse Red 60 peak then appears just after the solvent front. With this system 5 parts-per-million of disperse red dyes can be easily detected.

Analytical working curves for Disperse Red 60 and Disperse Red 55 have been developed by injecting 5, 10 and 20 part-per-million dye solutions in benzene/dimethyl formamide (99/1) in the chromatograph and eluting as described above. The curves are shown in Figure 1.

These results suggest that it should be possible to determine disperse red dyes in waste water quantitatively at less than 1 ppm with a ten-fold concentration step (resin column absorption) and separation and quantitation by liquid chromatography.

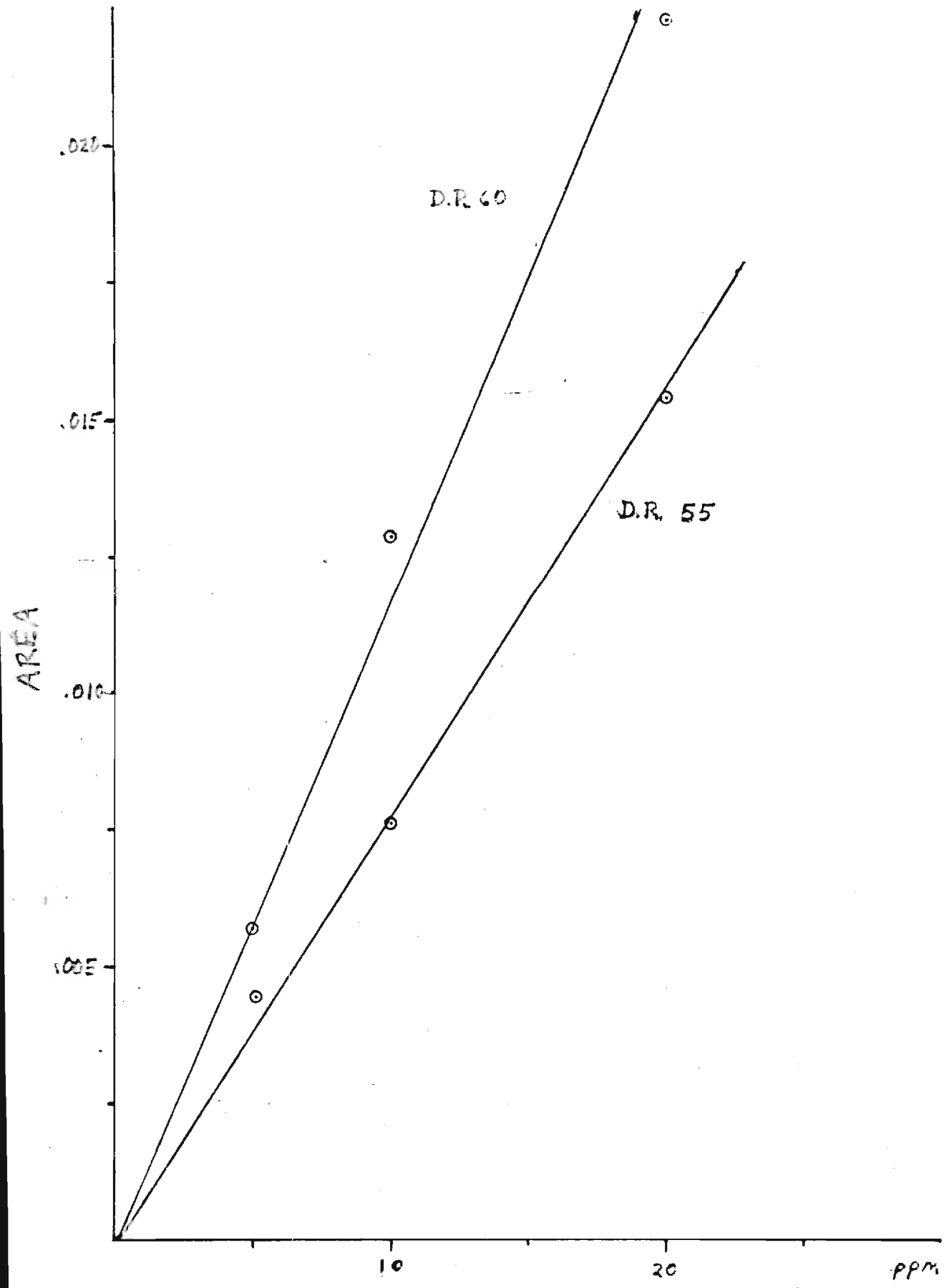
III. Sample Collection

Samples of the influent and effluent of the Dalton Wastewater Treatment Plant were obtained this month and have been put through the dye concentration system. No problems were encounted in concentration of the dyes.

These concentrates will be examined by liquid chromatography to confirm operation of the analytical system for disperse dyes.

IV. Future Work

Liquid chromatography studies on blue disperse dye and further work on recovery of acid dyes are planned for next month.


.020
.015
.010
.005
AREA
D.R. 60
D.R. 55
10
20
ppm

Monthly Progress Report Number 14
September 1 - October 1, 1976

Survey of Coosa Basin for Organic Contaminants from Carpet Processing

Environmental Protection Division
Department of Natural Resources
State of Georgia

Prepared Under Contract No.
E-27-630

by

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I. Introduction

Work has been completed this month on recovery and concentration of acid dyes from carpet processing wastewater. The recovery system and efficiencies for 15 of the most commonly used carpet dyes are described below.

II. Recovery and Concentration of Acid Dyes

Previous work on recovery and concentration of acid dyes using macroreticular resin (XAD-2) adsorption indicated that most acid dyes could be removed from the column in good yield by methanol extraction. However, several important acid dyes, including Acid Yellow 19, Acid Orange 128, and Acid Red 151, were not effeciently removed by the methanol. Other solvents have been investigated this month to improve the recovery of these difficult to remove acid dyes.

A number of solvents and solvent mixtures were studied including dimethylformamide, chloroform, tetrahydrofuran, ammonium hydroxide, acetic acid, and pyridine. The system which gave greatest recovery of the difficult to remove acid dyes was a mixture of pyridine, 1% ammonium hydroxide and tetrahydrofuran in a 40:20:40 ratio by volume. Elution of the adsorbed dye first with methanol and then with the solvent mixture gave greater than 70% recovery of all acid dyes. The complete concentration and recovery system is described in detail below.

III. Procedure for Concentration of Carpet Dyes

A. Column Preparation

Lab-Crest 9 mm by 500 mm chromatography columns equipped with either

demountable Teflon needle values (Lab-Crest 274-326) or demountable teflon stopcocks (Lab-Crest 274-461) were used in column preparation. Macroreticular resin (30 ml) of Type XAD-2 (Rohm and Haas Company) was slurried in approximately 60 ml of methanol and run through the column as rapidly as possible ($\sim$ 5 minutes). A glass wool plug was used in the bottom of the column to retain the resin. The column was then washed with 40 ml of benzene at approximately 2 bed volumes per hour. The benzene wash was followed by 40 ml methanol upflow wash at 8 bed volumes per hour to classify the column. The column was then washed with 40 ml of the pyridine, tetrohydrofuran, 1% ammonium hydroxide (40:40:20) solvent mixture at 4 bed volumes per hour and given a final wash with 200 ml of distilled water at 4 bed volumes per hour. The column was stored under distilled water until used. A total of approximately 30 ml was occupied by the resin.

B. Removal of Dyes from Wastewater

A 1000 ml Kelly infusion jar was attached to the top of the resin column with a 1 inch piece of silicone tubing of 0.1925 inches I.D. (Cole-Parmer). Wastewater (900 ml) and dimethylformamide (100 ml) were placed in the Kelly influsion jar and allowed to flow down the column at 4 bed volumes (120 ml) per hour. The dimethylformamide is added to increase the solubility of disperse dyes so that they will be adsorbed by the resin. If dye is present in the wastewater, colored bands will appear near the top of the column. After all the wastewater has passed through the column, the reservoir and column are washed with 50 ml of a 90% water-10% dimethylformamide mixture to insure that all of the wastewater sample has contacted the column.

C. Removal of Dyes from the Column

Since the dye is concentrated near the top of the column, the reservoir and stopcocks are removed and the column inverted for the subsequent elution steps. A 9 mm x 500 mm extension column is attached to the top to serve as a solvent reservoir. The column is first eluted with 40 ml benzene at approximately 2 bed volumes per hour. The disperse dyes are removed by benzene and the acid dyes remain on the column. The acid dyes are removed by first eluting with 40 ml of methanol followed by 40 ml of the pyridine, tetrahydrofuran, 1% ammonium hydroxide (40:40:20) mixture, both at a rate of 4 bed volumes per hour.

The benzene containing the disperse dyes is collected in a 50 ml round bottom flask equipped with a 24/40 ground glass joint. The flask is placed on a Buchi Rotavap R and benzene removed under aspirator vacuum at a temperature up to 100°C. The disperse dye is taken up in a 1% dimethylformamide - 99% benzene solvent and made up to 25 ml in a volumetric flask. This dye solution is now ready for injection in the liquid chromatograph for separation and quantitation. A increase in dye concentration of 900/25 or 36 is achieved by the resin adsorption.

The methanol and solvent mixture extracts are combined in a 250 ml round bottom flask and rotavrapped as described above for the benzene extracts. The residual acid dyes are taken up in 1% dimethylformamide - 99% methanol and made up to 25 ml. The acid dye solution can now be injected in the liquid chromatograph.

The recovery efficiencies for 1 part-per-million solutions of 15 important carpet dyes using the above procedure are shown in Table 1.

IV. Future Work

Tests of the dye recovery and analysis system on typical carpet dye waste samples are planned for next month.

Table 1

Recovery of Carpet Dyes From Wastewater
By Resin Adsorption

Acid Dyes		Disperse Dyes	
Acid Yellow 151	75%	Disperse Yellow 23	77%
Acid Red 337	75%	Disperse Yellow 3	98%
Acid Yellow 19	70%	Disperse Yellow 54	77%
Acid Yellow 135	100%	Disperse Red 60	89%
Acid Orange 128	76%	Disperse Red 55	95%
Acid Red 151	97%	Disperse Blue 7	73%
Acid Blue 25	80%	Disperse Blue 120	83%
Acid Blue 40	84%		

Monthly Progress Report Number 15
October 1 - November 1, 1976

Survey of Coosa Basin for Organic Contaminants from Carpet Processing

Environmental Protection Division
Department of Natural Resources
State of Georgia

Prepared Under Contract No.
E-27-630

by

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I. Introduction

Liquid chromatography work on separation and quantitation of disperse dyes has been completed with the development of methods for disperse blue dyes. This monthly report will be devoted to a summary of the analytical system for disperse dyes.

II. Quantitative Determination of Disperse Dyes in Dyeing Wastewater

Previous work on assessment of the quantities of dyes in textile processing wastewaters has relied on visual or spectrophotometric measurement of the color of the water sample. No techniques have been available to determine the concentrations of individual dyes present in the complex mixtures discharged by dyeing operations. The purpose of the present work was to develop systems for concentration and quantitation of individual dyes that are expected to be present in streams carrying carpet dyeing wastes.

Fifteen dyes were selected for initial study. Seven of these were disperse dyes (Yellow 23, Yellow 3, Yellow 54, Red 60, Red 55, Blue 7 and Blue 120). A resin adsorption system has been developed for concentration of the disperse dyes present in wastewater. The details of this procedure were reported last month (Monthly Progress Report Number 14) and will not be repeated here. A 36 fold increase in dye concentration was achieved by the resin adsorption step. This can be increased to 72, 108, or higher by increasing the volume of waste water passed through resin columns. The disperse dyes are taken up in a 99% benzene -1% dimethylformamide solvent at the end of the concentration step. This solution is used for subsequent separation and quantitation.

High pressure liquid chromatogarphy was selected as the anlytical system for separation and quantitation of dye mixtures. The chromatograph consists of a high pressure pump to maintain a flow of solvent through a tightly packed column, an injector to place a known volume of sample in the solvent flow, a column to separate the dyes by differential adsorption, and a detector to identify and quantitate the separated dyes. The detector used in this work was a variable wavelength UV-visible spectrophotometer. By operating in the visible region, dyes can be detected and quantitated in the presence of the many other organic compounds in dye wastewater which do not absorb strongly in the visible region. Similarly, selection of absorbing wavelength makes possible determination of, for example, yellow dyes even when blue dyes have not been completely separated. Thus, wavelength selection greatly simplifies the separation process.

The column selected for the separation of disperse dyes was the Partisil-10 PAC produced by Whatman. This column has cyano pendant groups on 10 μm silica particles and is especially effective for separating organic compounds of intermediate to high polarity. After much experimentation a solvent system utilizing tetrahydrofuran and cyclohexane was selected for separation of the disperse dyes.

A. Disperse Yellow Dyes

The column is first conditioned by pumping a 25/75 mixture of tetrahydrofuran/cyclohexane through the column for at least 15 minutes. An 8 μl sample of the dye mixture is injected in the solvent stream and the effluent of the column monitored at 420 nm. The composition of the solvent varied

linearly from 25/75 to 100/0 tetrahydrofuran/cyclohexane over a 15 minute period. The solvent flow rate was 1 ml/minute. The resulting chromatograms of a standard 5, 10 and 20 ppm mixture of disperse yellow 3, 42, and 54 are shown in Figure 1. The disperse yellows are well separated and excellent linear curves are obtained when the areas under the peaks are plotted versus concentration.

It is interesting to note that disperse yellow 23 gives several peaks. This dye is undoubtedly a mixture of several compounds which are partially separated by the chromatograph.

B. Disperse Red Dyes

Two separate runs on the chromatograph were required to analyze for the disperse red dyes at very low concentrations. The probable reason for this was that the red dyes are a mixture of compounds and when long elution times were used the peaks split into many components which reduced the sensitivity.

The following procedure was used with the red dyes. The column was equilibrated for 15 minutes with an 80/20 tetrahydrofuran/cyclohexane solution. Eight µl of dye were injected and the effluent monitored at 520 nm. A flow rate of 1 ml/minute was used. Under these conditions disperse red 55 elutes with the solvent front and disperse red 60 approximately 1 to 2 minutes after the solvent front. The column is then equilibrated with a 35/65 mixture of tetrahydrofuran/cyclohexane and 8 µl of the dye mixture again injected. Under these conditions disperse red 55 elutes just after the solvent front and disperse red 60 is retained on the column. Typical chromatograms for 5, 10 and 20 ppm disperse red 55 are shown in Figure 2. Very similar results were

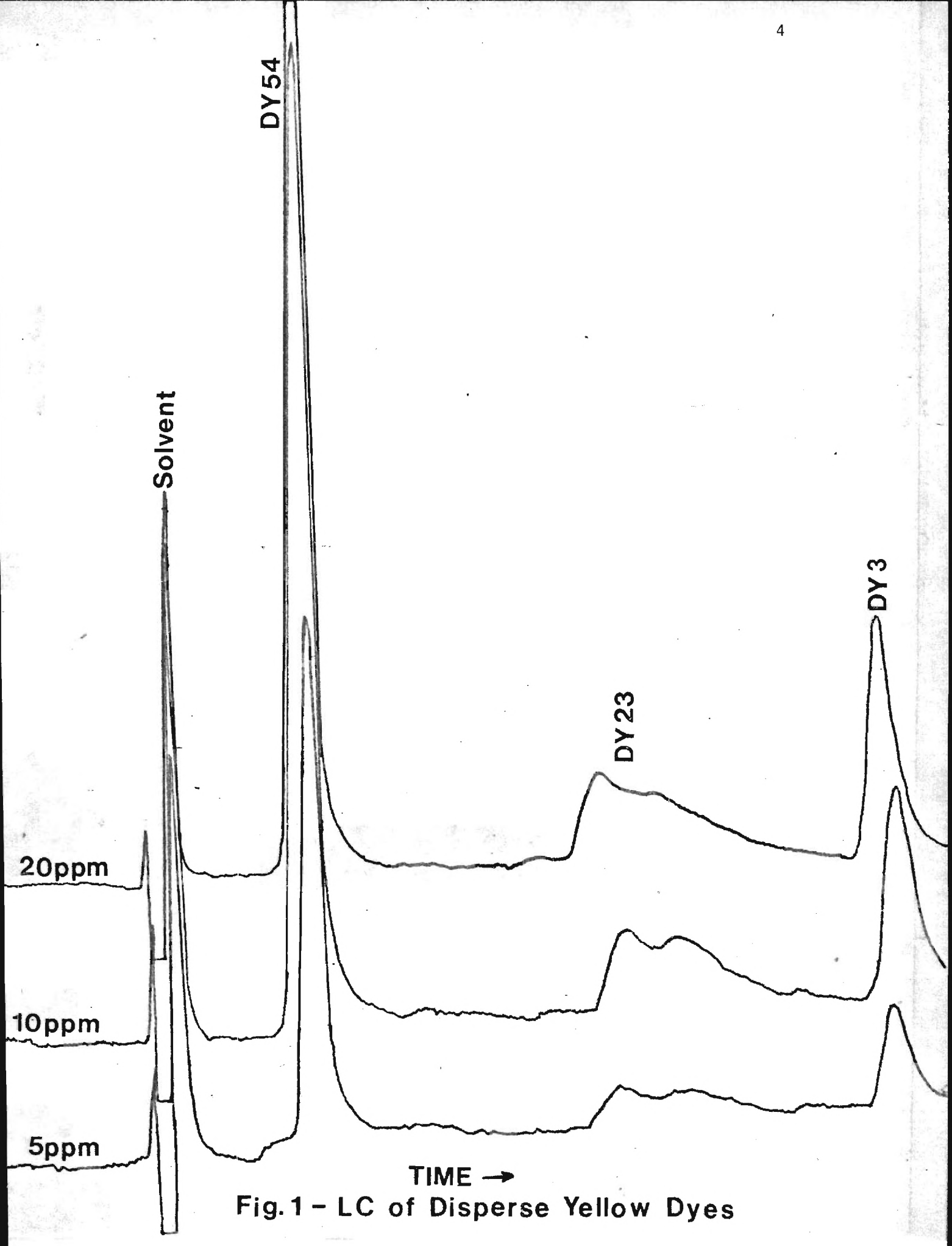

Fig. 1 – LC of Disperse Yellow Dyes

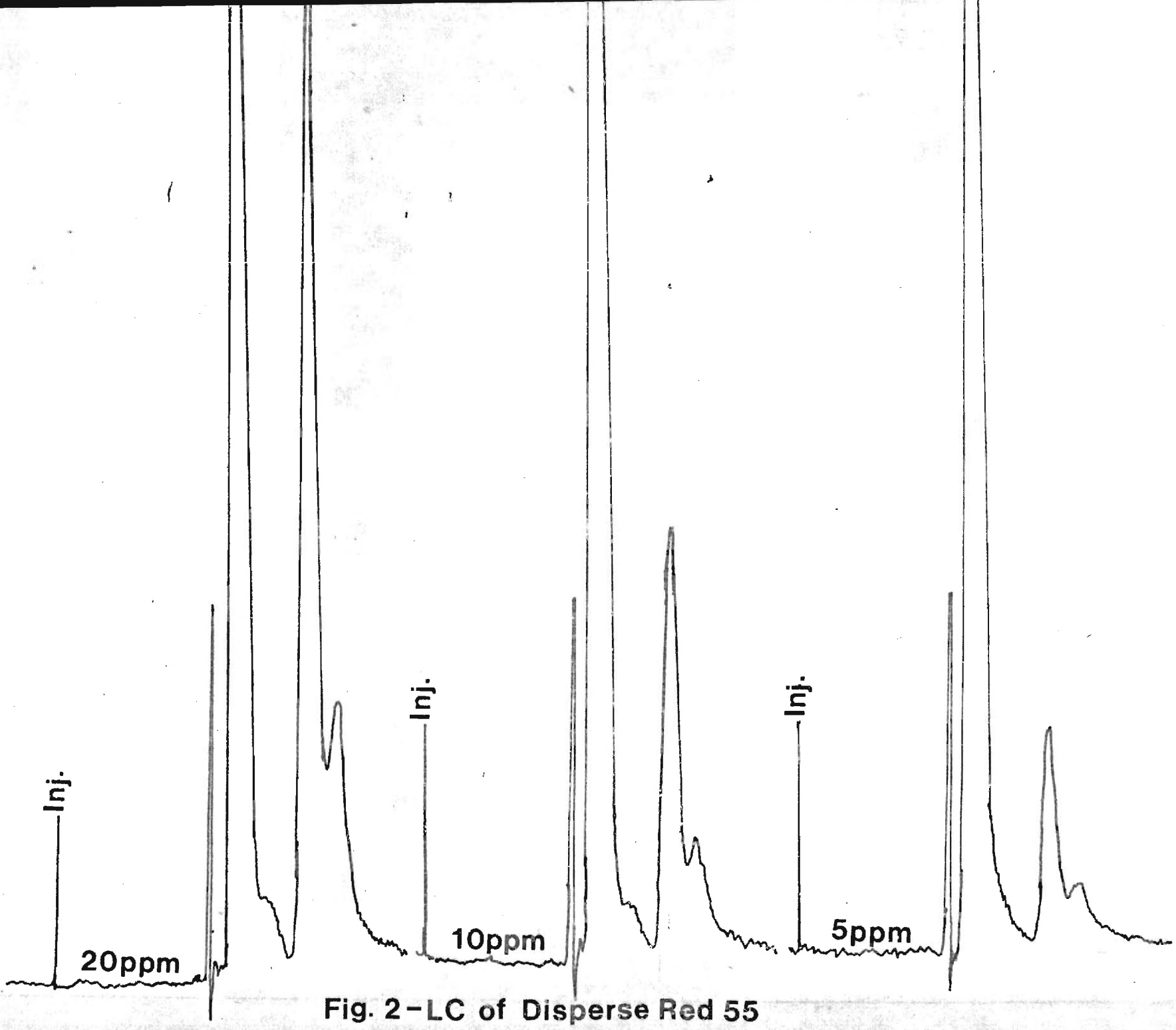

Fig. 2 – LC of Disperse Red 55

obtained for disperse red 60. It should be noted that the detector was not set at its highest sensititvity in recording Figure 2. At highest sensitivity 1 ppm of the disperse red dyes should be very readily detected and analyzed.

C. Disperse Blue Dyes

A system similar to the one used for the disperse red dyes was used in analysis of dipserse blue dyes. The column is equilibrated with 100% tetrahydrofuran at a flow rate of 1 ml/min. A 8 µl sample of the dye mixture is injected and the effluent monitored at 620 nm. The chromatogram shows a number of peaks indicating that the dye contains several components but two very distinct peaks are observed at about 2 and 4 minutes retention time. A chromatogram of a 20 ppm solution of disperse blue 7 is shown in Figure 3. Under these conditions disperse blue 120 elutes with the solvent front.

Disperse blue 120 is determined by equilibrating the column with a 45/55 tetrahydrofuran/cyclohexane mixture and eluting with this mixture. Several peaks are observed with the principal peak at about 2 minutes retention time. Under these conditions disperse blue 7 is retained by the column thus providing a separation of the two blue dyes.

III. Future Work

Analytical development work for the disperse dyes is essentially complete. Results on carpet mill effluents and samples containing known mixtures of dyes and dyeing chemicals will be reported next month.

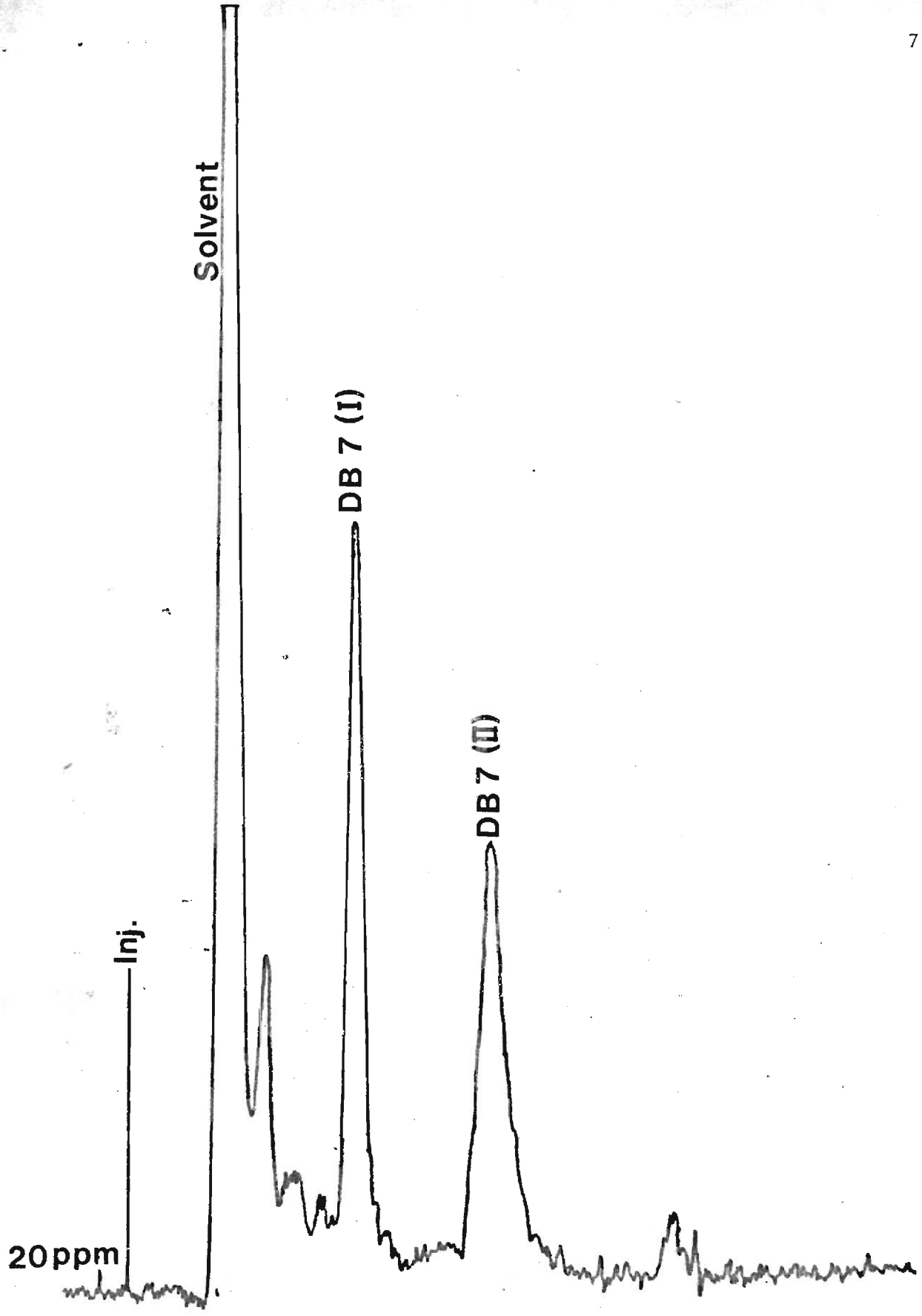

Fig. 3 - LC of Disperse Blue 7

Monthly Progress Report Number 16
November 1 - December 1, 1976

Survey of Coosa Basin for Organic Contaminants from Carpet Processing

Environmental Protection Division
Department of Natural Resources
State of Georgia

Prepared Under Contract No.
E-27-630

by

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I. Introduction

Effort this month has been directed toward initial tests of the analytical system for disperse dyes on known dye mixtures. Results of initial tests on effluent samples are also reported.

II. Performance of Analytical System for Disperse Dyes

The procedures for determining the concentration of disperse dyes in complex mixtures developed in the last few months have been employed on several typical carpet waste samples containing known quantities of disperse dyes. This typical waste sample was prepared by dissolving appropriate quantities of the chemicals given in Table 20 of the report "Chemical Use and Discharge in Carpet Piece Dyeing" (Final Report Project E-27-626, Georgia Institute of Technology, September 1975) in water. The sample contained not only dyes but the auxiliaries, finish components, pH control agents and other organic and inorganic compounds commonly present in dye wastewater. The quantities of each of 6 disperse dyes present in the sample are given in Table 1.

One liter of the synthetic waste sample was concentrated using the column procedure described in Monthly Report 14. The concentrate was injected in the liquid chromatograph as described in Monthly Report 15. The quantities of each of the six dyes found in the known waste sample are given in Table 1 as well as the per cent of the known that was found. Results indicate that greater than 70% of most disperse dyes are detected. In the case of disperse blue 7 (65%) and disperse yellow 23 (66%) the dye gives several peaks in the chromatogram indicating that a number of compounds are present in the "pure" dye. The large number of peaks observed reduces the senstitivity to these particular dyes.

The known waste sample described above was also exposed to a biological treatment systems (Horizons, Inc.) and the effluent of the treatment system analyzed for dye content to determine if the system could detect and quantitate dyes at levels expected in waste treatment plant effluents. Results for Disperse Red 55 are shown in Table 2 for ten analyses of the effluent. Similar data for disperse yellow 3 are shown in Table 3.

A sample of effluent was obtained from the Dalton Waste Treatment Plant on October 28, 1976 at approximately 4:15 P.M. This is the time at which the plant experiences its maximum flow. The sample was analyzed as described previously and yielded the results shown in Table 4. Results for the Horizon Biooxidation Unit are also shown for comparison with the Dalton Waste Treatment Plant data. The ranges in the Horizon Unit data are total ranges obtained by analysis of 10 effluent samples. The per cent of each dye removed by biological oxidation is shown in the last column of Table 4.

Disperse yellow 3 and disperse yellow 23 were below the limits of detectability in the Dalton Waste Treatment Plant sample. Results from the bench unit suggest that disperse yellow 3 may be readily removed by the waste treatment system (93%). This may explain why it is not observed in plant effluents. The detection limit for disperse yellow 23 (due to the fact that it is a mixture of compounds) may be responsible for our inability to detect it in this sample.

One sample of the Conasanga River at Looper's Bend bridge was also obtained and has been concentrated. The analysis has not been completed but the column extracts suggest that acid dye concentrations are much higher than disperse dye concentrations in the river sample.

III. Future Work

Completion of the analysis system for acid dyes will be the major effort next month.

TABLE 1

Dye	Conc. in Waste Known (mg/L)	Conc. in Waste Found (mg/L)	% Found
DY 54	5.67	4.05	70
DY 3	5.78	5.31	92
DY 23	8.21	5.44	66
DR 60	3.97	3.44	87
DR 55	1.82	1.27	70
DB 7	1.82	1.18	65

TABLE 2

Sample	Conc. mg/L	% Removed by Biological Treatment
1	2.46	28
2	2.77	19
3	1.48	57
4	1.33	61
5	0.88	74
6	0.48	86
7	1.42	59
8	1.22	65
9	1.06	69
10	0.84	76
	Average	59

TABLE 3

Disperse Yellow 3 in Biologically Treated Dye Waste

Sample	Conc. (mg/l)	% Removed by Biological Treatment
1	0.95	82
2	0.53	90
3	0.37	93
4	0.37	93
5	0.21	96
6	0.16	97
7	0.22	96
8	0.32	94
9	0.16	97
10	0.32	94
	Average	93

TABLE 4

Analysis of Dalton Waste Treatment Plant
Effluent for Disperse Dyes
Compared to Bench Unit Effluent

Dye	DWTD Concentration (mg/l)	Bench Unit Concentration (mg/l)	% Removed Bench Unit
Disperse Red 55	1.95	0.11 - 0.62	78
Disperse Red 60	3.40	0.48 - 2.77	59
Disperse Blue 7	0.57	0.16 - 0.66	64
Disperse Yellow 54	2.30	0.68 - 1.45	77
Disperse Yellow 3	—	0.16 - 0.95	93
Disperse Yellow 23	—	1.47 - 2.34	66

Monthly Progress Report Number 17
December 1, 1976 - January 1, 1977

Survey of Coosa Basin for Organic Contaminants from Carpet Processing

Environmental Protection Division
Department of Natural Resources
State of Georgia

Prepared Under Contract No.
E-27-630

by

Wayne C. Tincher
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I. Introduction

Effort this month has been directed primarily at development of high pressure liquid chromatography techniques for separation and quantitation of acid dyes used in carpet production.

II. Analytical Procedures for Acid Dyes

Acid dyes used in dyeing carpets and other textile products of nylon and wool usually contain one or more sulfonate groups, generally as the sodium salt. Samples containing such ionic species have traditionally been separated by ion exchange chromatography. There are many problems with this type of separation in control and reproducibility of the chromatographs. For separation of acid dyes a new liquid chromatography variation, paired ion chromatrography (PIC), was investigated. This technique has been used previously for dye separations (Wittmer, D.P., Nuessle, W.D. and Haney, W.G., Anal. Chem. 47, 1422; 1975) and similarities in structures of the dyes in the literature reference and dyes of interest in the present work suggested that PIC might be applicable to acid dye separation.

In the PIC technique dye mixtures dissolved in methanol (from the resin column concentration step) are injected in the liquid chromatograph. A silica gel column with C_{18} hydrocarbon chains bonded to the surface (Reeve Angel ODS-2) is used for separation. The dyes are eluted with mixtures of methanol and water in which tetrabutylammonium phosphate is dissolved (PIC Reagent A, Waters Associates). In general, gradient elution is used to separate the various dyes.

Preliminary experiments using the PIC technique were conducted on mixtures of yellow acid dyes. After several trials it was found that a gradient beginning at 60/40 (methanol/water) and increasing to 85/15 over a 10 minute period gave good separation of the yellow dyes. A flow rate of 1 ml/minute was used and the detector was set at 420 nm. The chromatogram is shown at the top of Figure 1. The sample was 8 ml of a 10 ppm solution of Acid Yellow 19, Acid Yellow 135 and Acid Yellow 151.

A similar chromatogram of two acid red dyes (Acid Red 151 and Acid Red 337) and Acid Orange 128 are shown at the bottom of Figure 1. Conditions were identical for the acid reds except that the detector was set at 520 nm.

Preliminary experiments also indicate that the same solvent gradient will also separate acid blue dyes. Thus, one set of conditions can be used for all acid dyes.

III. Future Work

Quantitation of the acid dye analysis system will be carried out next month.

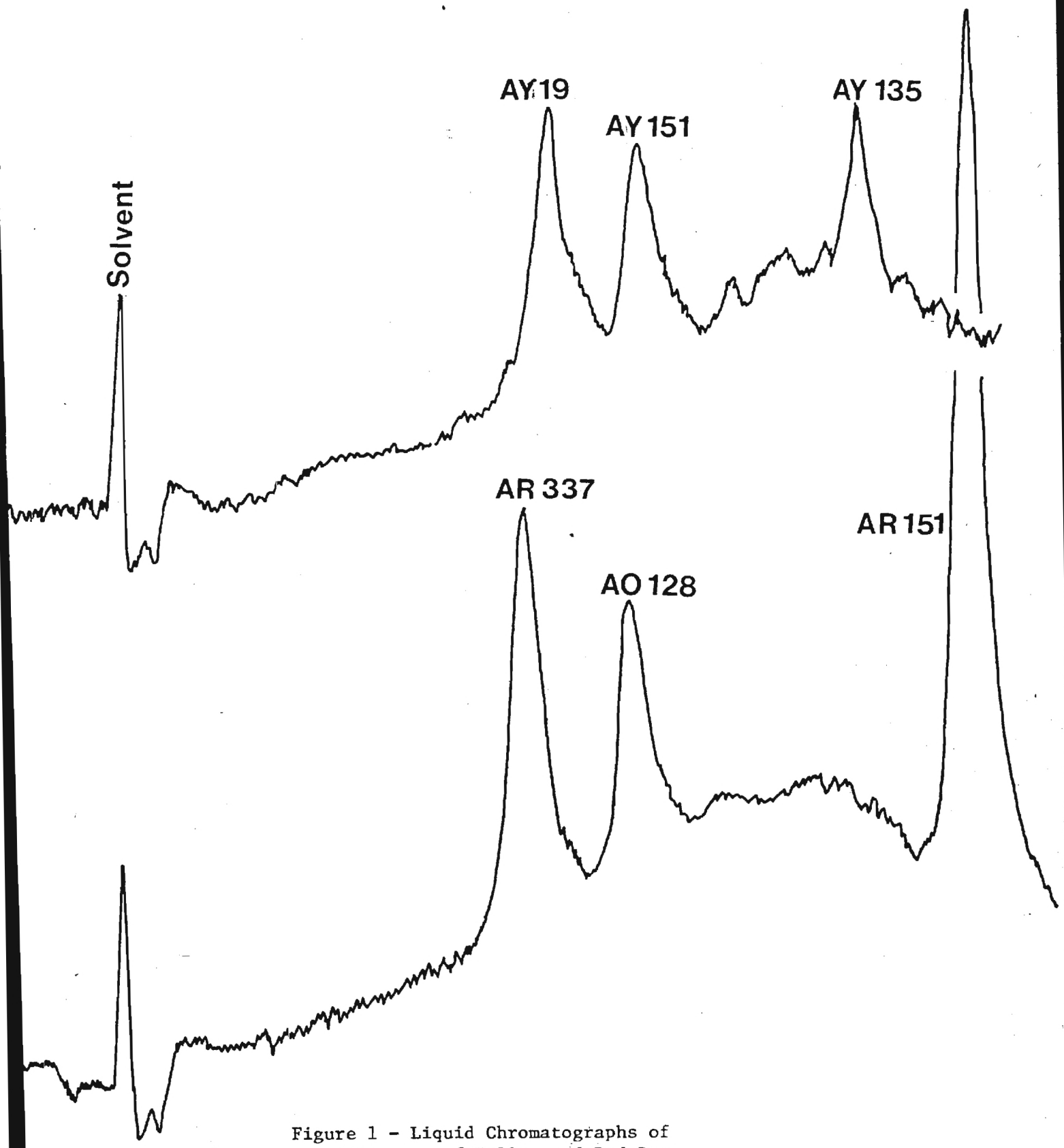

Figure 1 - Liquid Chromatographs of
Mixtures of Yellow and Red Dyes

Monthly Progress Report Number 18
January 1, 1977 - February 1, 1977

Survey of Coosa Basin for Organic Contaminants from Carpet Processing

Environmental Protection Division
Department of Natural Resources
State of Georgia

Prepared Under Contract No.
E-27-630

by

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I. Introduction

Effort this month has been directed toward completion of development of high pressure liquid chromatography techniques for separation and quantitation of acid dyes used in carpet production.

II. Separation of Acid Blue Dyes

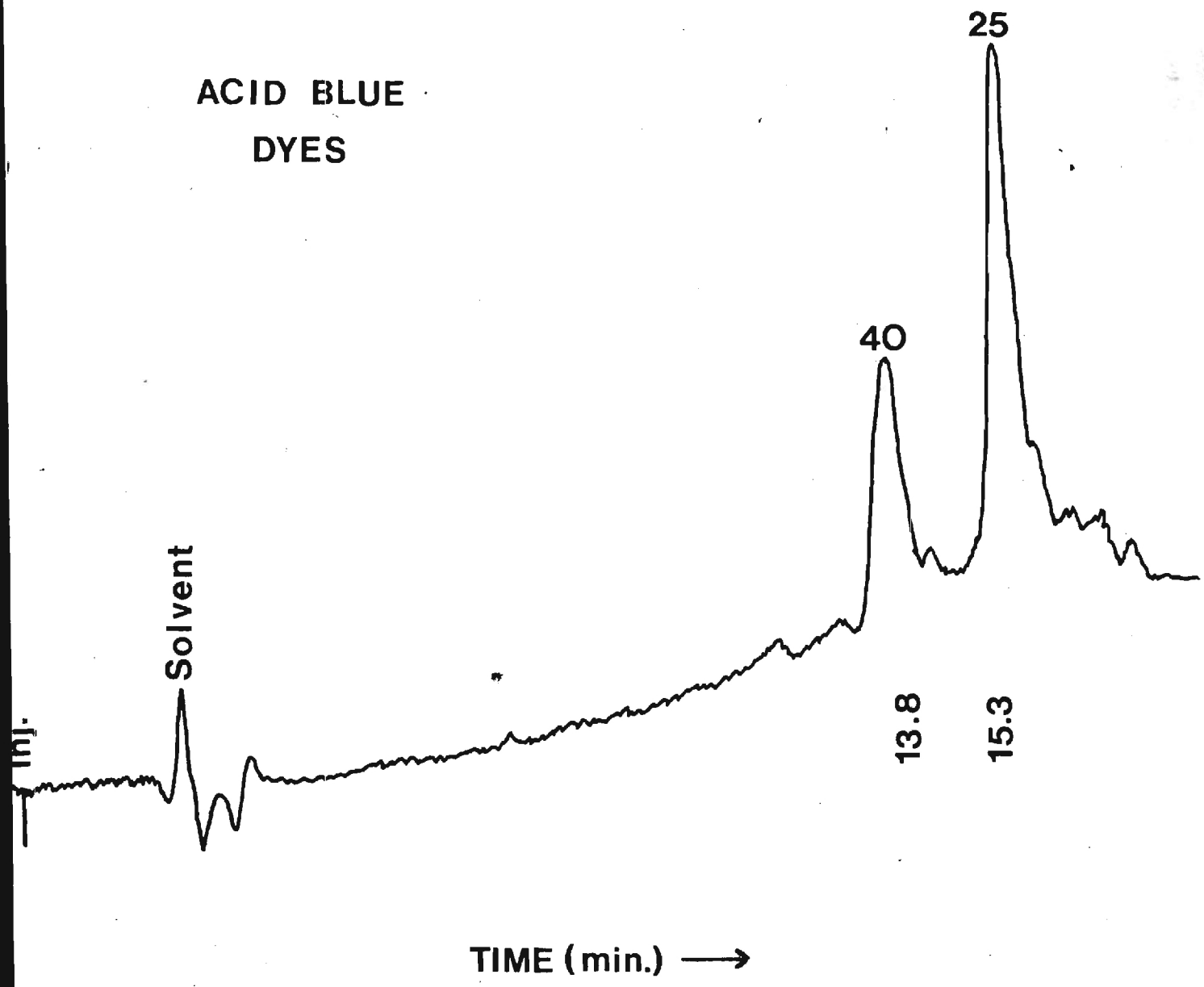
A separation scheme for acid red and acid yellow dyes was reported last month. This scheme utilized a reverse phase separation using paired ion chromatography techniques. A similar procedure has been employed for separation of acid blue dyes. The blue dyes in a methanol 99% - DMF 1% solution were injected in the liquid chromatograph and eluted with a methanol-water gradient (60:40 methanol:water to 85:15) over a 10 minute period with monitoring of the effluent at 615 nm. An ODS-2 Column was used for the separation. A chromatigram of a 10 part-per-million solution of Acid Blue 25 and Acid Blue 40 is shown in Figure 1. The two dyes are well separated at 13:8 and 15:3 minutes retention time.

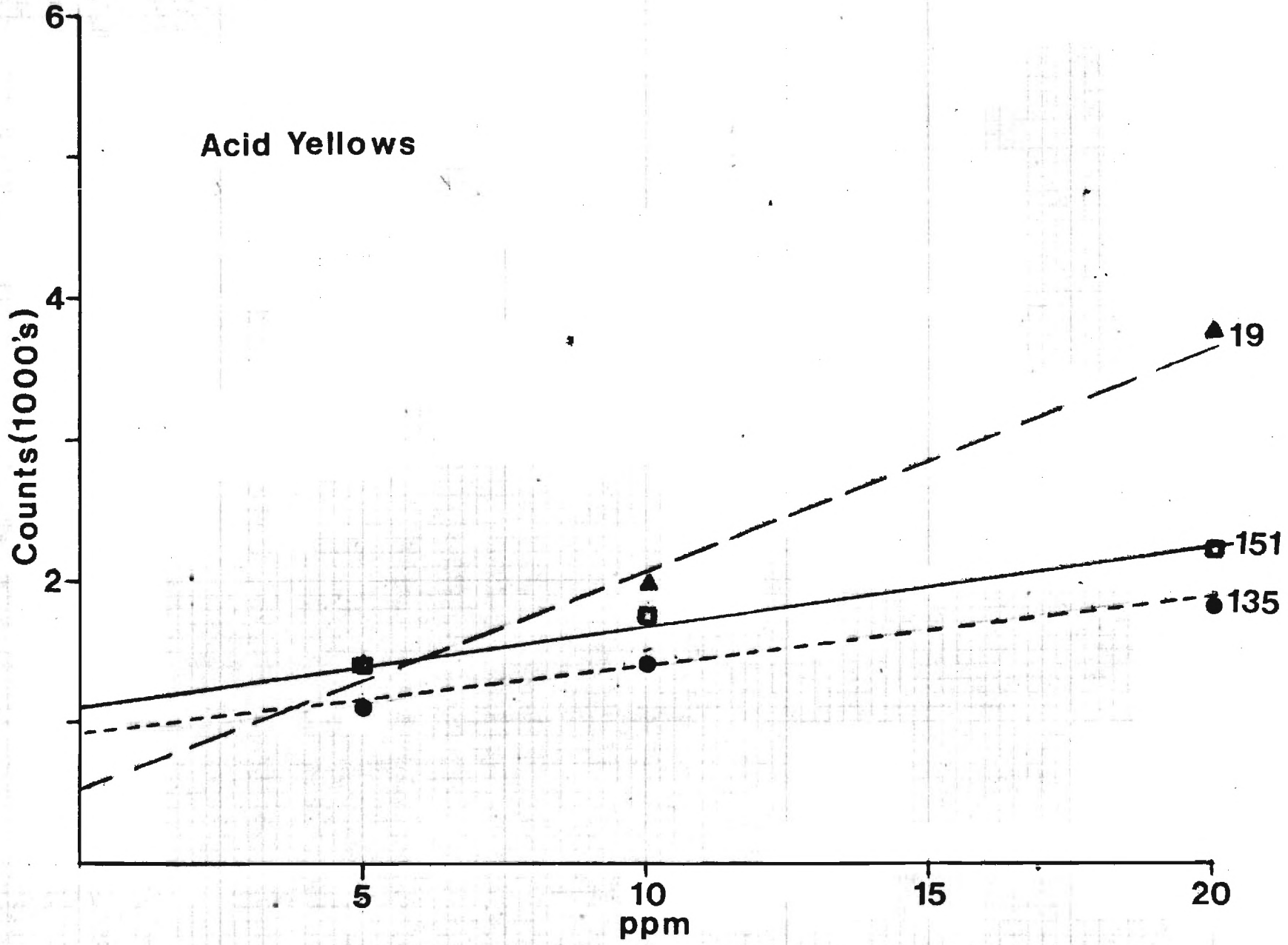
III. Analytical Working Curves

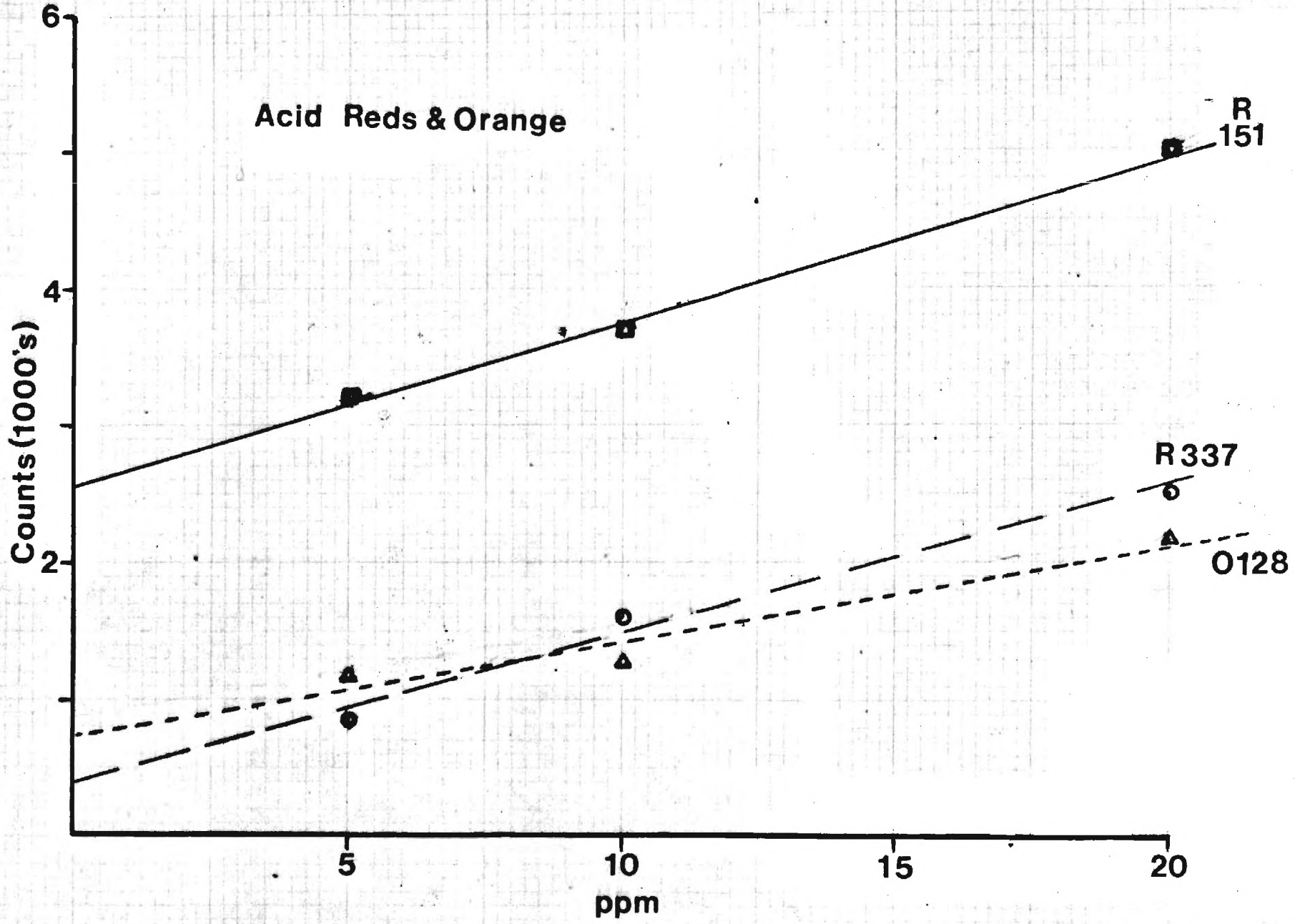
Using the techniques described in the December monthly report, 5, 10 and 20 ppm standard solutions of acid dyes were prepared and separated by liquid chromatography. The visible light absorption was measured at 420 nm for the yellow dyes, at 520 nm for the red and orange dyes and at 615 nm for the blue dyes. The curves obtained are shown in the three attached figures. Areas were obtained with an electronic integrator (Counts) and plotted versus concentration. Computer analyses of the results gave regression coefficients very near unity indicating that very linear curves were obtained.

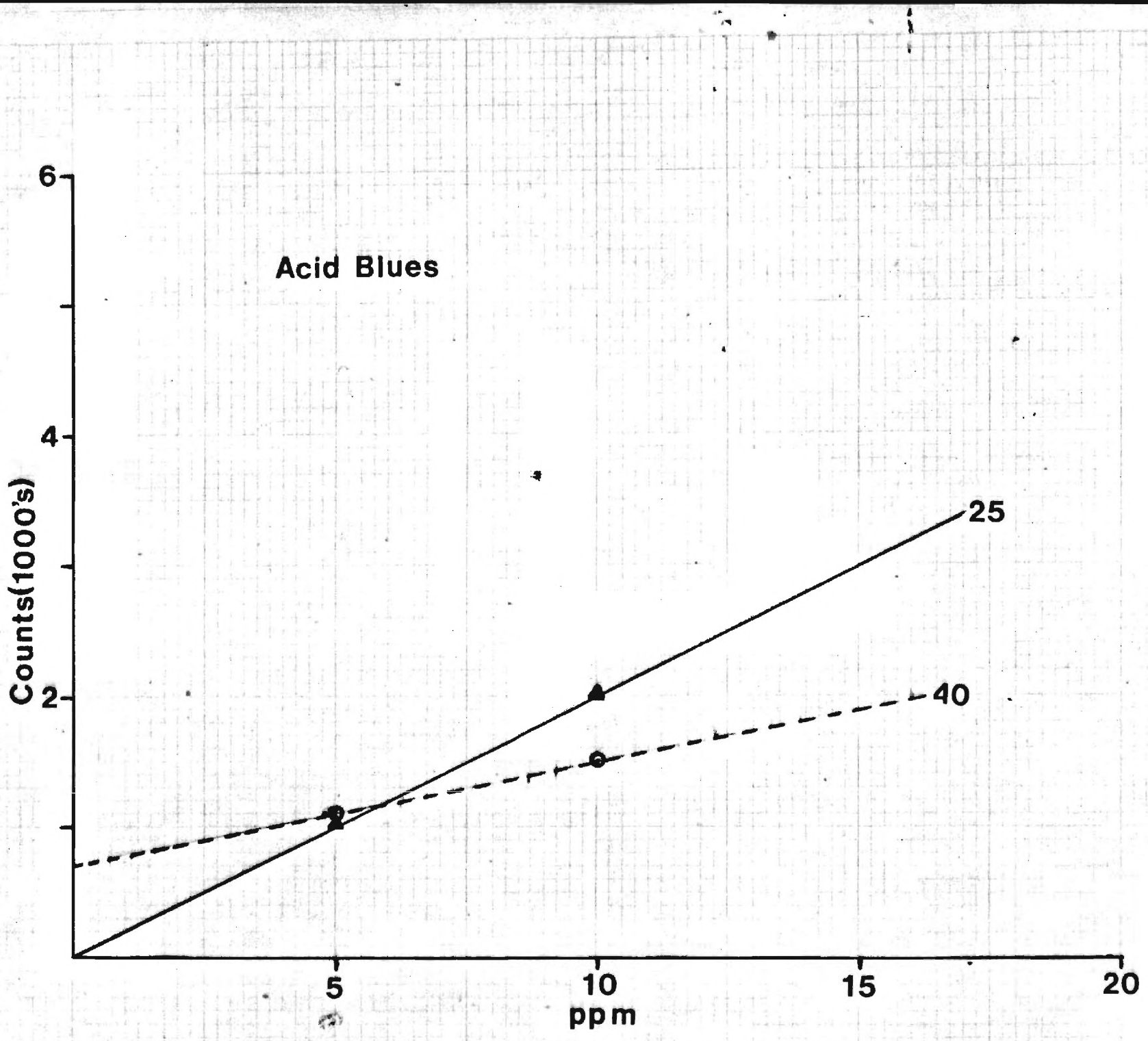
IV. Future Work

Analysis of some known dye solutions and some modifications of the developed procedures will be carried out next month in preparation for analyses of stream samples.


ACID BLUE
DYES
25
40
Solvent
Inj.
13.8
15.3
TIME (min.) ⟶


Acid Yellows
Counts(1000's)
6
4
2
5
10
15
20
ppm
19
151
135


Acid Reds & Orange
R 151
R 337
O128
Counts (1000's)
6
4
2
5
10
15
20
ppm


Acid Blues
Counts(1000's)
6
4
2
25
40
5
10
15
20
ppm

Monthly Progress Report Number 19
February 1, 1977 - March 1, 1977

Survey of Coosa Basin for Organic Contaminants from Carpet Processing

Environmental Protection Division
Department of Natural Resources
State of Georgia

Prepared Under Contract No.
E-27-630

by

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I. Some minor modifications in the analytical scheme for acid dyes and improvement in concentration procedures have been carried out this month. These modifications are described below.

II. Acid Orange 128

Acid Orange 128 is the only color in the selected list of dyes that is not a primary color. As a result Acid Orange 128 has strong absorption in both the red and yellow regions of the visible spectrum. This situation creates no problem in analysis of the red dyes since Acid Orange 128 is well separated from Acid Red 337 and Acid Red 151 (see Figure 1). However, in the analysis of the yellow dyes, Acid Orange 128 is not separated from Acid Yellow 151. Two approaches were considered for solution of this problem. First, the election solvent program for the yellow dyes could have been changed. This approach was not selected as it would make an otherwise very simple analytical scheme for acid dyes more complex. The second approach and the one selected was to correct the AY 151 absorption for the Acid Orange 128. In this scheme the concentration of Acid Orange 128 is determined from the adsorption at 520 nm. From the concentration and the known absorptivity at 420 nm the contribution of Acid Orange 128 at 420 nm can be substracted to obtain the true absorption due to Acid Yellow 151.

All the other acid dyes have been examined spectrophotometrically to determine if any other similar interferences are present. Acid Orange 128 was the only problem found.

III. Concentration Procedures

In previous work concentration of wastewater samples has been carried out by passing .9 or 1.8 liters of wastewater through an XAD-2 resin column and concentrating the solvent extract by evaporation to 25 ml. This gives a concentration factor of either 36 or 72. Recent experiments have shown that the column extracts can be concentrated to 10 ml to give a concentration factor of 90 or 180. Using the larger volume of sample and the concentration to 10 ml, any of the 15 dyes can be determined at 25 parts-per-billion. Some of the dyes can be determined at 5 part-per-billion. The limiting factor is the number of components that are present in the dye. For example, Disperse Blue 120 gives at least three major peaks in the liquid chromatogram. This results in somewhat less sensitivity for these two dyes.

IV. Future Work

A major sampling trip is planned for next month.

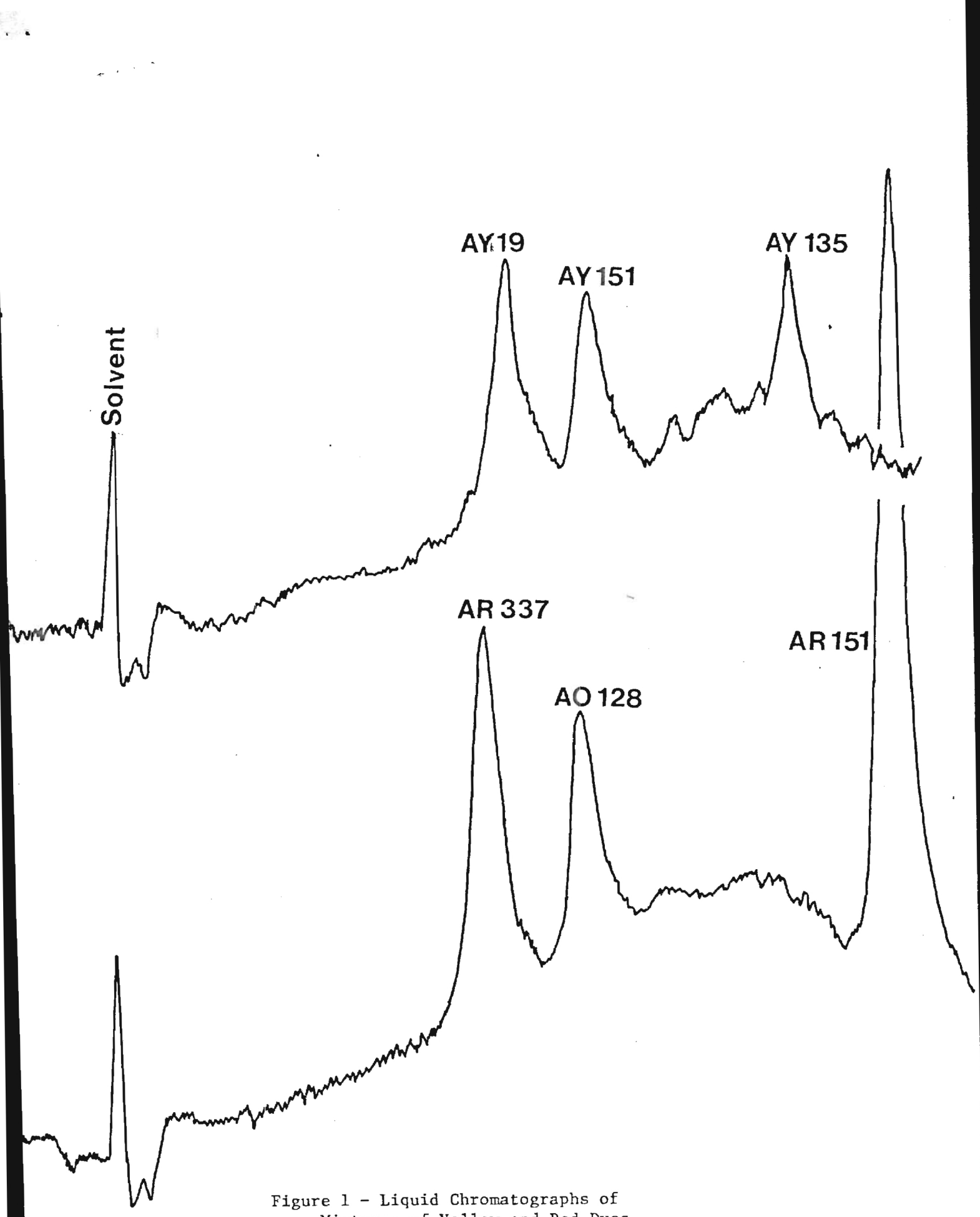

Figure 1 - Liquid Chromatographs of
Mixtures of Yellow and Red Dyes

Monthly Progress Report Number 20

March 1, 1977 - April 1, 1977

Survey of Coosa Basin for Organic Contaminants from Carpet Processing

Environmental Protection Division
Department of Natural Resources
State of Georgia

Prepared Under Contract No.
E-27-630

by

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I. Introduction

Major effort this month has been directed toward collection of samples from the Coosa Basin for concentration and analysis.

II. Flow Times for Coosa Basin

The peak period in dyeing of carpet in the Dalton area runs during the day shift on Mondays through Thursdays. This results in a peak flow at the Dalton Waste Treatment Plant usually between 3 and 5 in the afternoon of those days. Friday is generally a "clean-up" day and most plants are closed on weekends except during peak periods of production. An attempt was made to collect samples in the Coosa Basin at times such that the samples would reflect the peak flows at the Dalton Waste Treatment Plant and contain maximum dye concentrations.

Mr. Gary Ellis of the Environmental Protection Division provided us with flow times in the Coosa Basin based on a computer simulation of stream flow. Volumes and flow times based on this model for the week of March 7 are shown in Table 1.

III. Sample Collection

During the week selected for sampling the carpet industry in Dalton was operating at 80 - 90% of normal production capacity based on total flow at the Dalton Waste Treatment Plant. Residence time in the Dalton Waste Treatment Plant is approximately 24 hours. The effluent on any given day is therefore representative of the influent received the previous day.

The day and hour of collection at the various sites is shown in Table 2. The table also gives the estimated time that the sample was entering the Dalton Waste Treatment Plant. The sample collected at the Georgia Highway 40 bridge over the Oostanula River was collected at a time such that the sample was entering the Calhoun Waste Treatment plant Tuesday, March 8 at approximately 2:00 P.M.

All samples were refrigerated at the collection site and were kept at 0°C until the concentration step. Several of the samples have been concentrated and, as noted earlier, acid dyes appear to be present in greater concentration than disperse dyes.

IV. Future Work

Samples will be concentrated and prepared for analysis next month.

Table 1

Flow Times in Coosa Basin

Site	Flow	Time
Dalton Water Intake	-	0
Tibbs Bridge	52 cfs	13 - 15½ hours
Dalton Waste Treatment Outfall	-	12 - 14½ hours
Looper's Bridge	789 cfs	1 hour
Tilton's Bridge	884 cfs	15 - 18½ hours
Calhoun Water Intake	2550 cfs	22 - 26½ hours
Rome Water Intake	2640 cfs	30 - 35 hours

Table 2

Sample Collection Times

SITE	TIME COLLECTED	TIME ENTERED DALTON WASTE TREATMENT PLANT
Dalton Waste Treatment Plant Influent	Wed., Mar. 9, 4:00 PM	Wed., Mar. 9, 4:00 PM
Dalton Waste Treatment Plant Effluent	Wed., Mar. 9, 4:20 PM	Tues., Mar. 8, 4:00 PM
Looper's Bridge	Wed., Mar. 9, 5:00 PM	Tues., Mar. 8, 4:00 PM
Tilton Bridge	Thurs., Mar. 10, 9:00 AM	Tues., Mar. 8, 4:00 PM
Calhoun Raw Water	Thurs., Mar. 10, 10:00 AM	Mon., Mar 7, 4:00 PM
Calhoun Finish Water	Thurs., Mar. 10, 10:30 AM	Mon., Mar. 7, 4:00 PM
Calhoun Filter Backwash	Thurs., Mar. 10, 11:00 AM	Mon., Mar. 7, 4:00 PM
Calhoun Waste Treatment Plant Influent	Thurs., Mar. 10, 12:30 PM	—— ——
Calhoun Waste Treatment Plant Effluent	Thurs., Mar. 10, 12:50 PM	—— ——
Georgia Highway 40 Bridge (Oostanaula)	Thurs., Mar. 10, 2:00 PM	—— ——

Monthly Progress Report Number 21

April 1, 1977 - May 1, 1977

Survey of Coosa Basin for Organic Contaminants from Carpet Processing

Environmental Protection Division
Department of Natural Resources
State of Georgia

Prepared Under Contract No.
E-27-630

by

Wayne C. Tincher
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I. Introduction

Major effort this month has been directed toward concentration and analysis of samples collected in the Coosa Basin last month. A list of samples under analysis is shown in Table 1.

II. Analysis of Coosa Basin Samples

The samples listed in Table 1 have been concentrated by the XAD-2 resin technique and taken up in 10 ml of benzene for the disperse dye fraction and 10 ml of methanol for the acid dye fraction. The concentration factor was 180 (1800 ml to 10 ml). Visual observation of the extracts show that more acid dye is present in the various samples than disperse dye. Apparantly, the disperse dyes are more readily removed by waste treatment than the acid dyes. The extracts range in color from dark brown to almost water white.

Samples have been analyzed for several of the disperse dyes (Blue 7, Blue 120, Red 60) and these results will be reported at the completion of the disperse dye analysis.

III. Future Work

Delivery is expected next month of the new High Pressure Liquid Chromatograph. Availability of this equipment should permit more efficient analysis of the collected samples. A second sampling trip is also planned.

TABLE 1

Coosa Basin Samples Collected

Sample	Collection Site	Time of Collection	
129-10-2	Dalton Raw Water Intake	10/28/76	11:45 A.M.
129-11-5	Dalton Waste Treatment Plant Influent	10/28/76	3:15 P.M.
129-11-8	Dalton Waste Treatment Plant Effluent	10/28/76	4:15 P.M.
129-12-9	Looper's Bridge	10/28/76	5:15 P.M.
129-22-1	Dalton Waste Treatment Plant Influent	3/9/77	4:00 P.M.
129-22-2	Dalton Waste Treatment Plant Effluent	3/9/77	4:20 P.M.
129-22-3	Looper's Bridge	3/9/77	4:45 P.M.
129-23-4	Tilton Bridge	3/10/77	9:00 A.M.
129-23-5	Calhoun Raw Water Intake	3/10/77	10:00 A.M.
129-23-6	Calhoun Finish Water	3/10/77	10:30 A.M.
129-23-7	Calhoun Filter Backwash	3/10/77	11:00 A.M.
129-23-8	Calhoun Waste Treatment Plant Influent	3/10/77	12:30 P.M.
129-23-9	Calhoun Waste Treatment Plant Effluent	3/10/77	12:50 P.M.
129-23-10	Oostananla Bridge at Ga. Highway 140	3/10/77	1:45 P.M.

Monthly Progress Report Number 22

May 1, 1977 - June 1, 1977

Survey of Coosa Basin for Organic Contaminants from Carpet Processing

Environmental Protection Division
Department of Natural Resources
State of Georgia

Prepared Under Contract No.
E-27-630

by

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I. Introduction

Major effort this month has been directed toward analysis of samples collected on 10/28/76, 3/9/77 and 3/10/77 in the Coosa River Basin.

II. Analysis of Coosa Basin Samples

Samples collected at the Dalton and Calhoun waste treatment plants and at various sites on the Conasauga and Oostanaula Rivers have been concentrated and analyzed for 7 disperse dyes. A list of the samples collected is given in Table 1. Results of the analysis are given in Table 2.

Results of the analysis for disperse dyes suggest that concentrations are quite low at Looper's Bridge (129-22-3) and Tilton Bridge (129-22-4) and in the Calhoun water supply (129-23-5, 129-23-6, 129-23-7). Disperse dye levels in these samples were at the very lowest limit of detectability of the procedure.

The effectiveness of typical waste treatment systems for disperse dyes can be inferred by a comparison of the influent to the Dalton waste treatment plant (129-23-1) and the effluent (129-22-2) and the influent (129-23-8) and effluent (129-23-9) of the Calhoun waste treatment plant. Caution must be used in making these comparisons since the samples represent different days of carpet production and some variability in dye use from day to day would be expected. However, data from both waste treatment plants suggest that Disperse Red 60, Disperse Yellow 54, and Disperse Blue 120 are not readily removed in the treatment plants. Significant removal of Disperse Red 55, Disperse Yellow 3, and Disperse Yellow 23 apparantly occurs in waste treatment. It will be interesting to see if additional data support these preliminary observations.

III. Future Work

A third trip is planned for early June to collect samples during the current period of low flow in the Coosa Basin.

TABLE 1

Coosa Basin Samples Collected

Sample	Collection Site	Time of Collection	
129-10-2	Dalton Raw Water Intake	10/28/76	11:45 A.M.
129-11-5	Dalton Waste Treatment Plant Influent	10/28/76	3:15 P.M.
129-11-8	Dalton Waste Treatment Plant Effluent	10/28/76	4:15 P.M.
129-12-9	Looper's Bridge	10/28/76	5:15 P.M.
129-22-1	Dalton Waste Treatment Plant Influent	3/9/77	4:00 P.M.
129-22-2	Dalton Waste Treatment Plant Effluent	3/9/77	4:20 P.M.
129-22-3	Looper's Bridge	3/9/77	4:45 P.M.
129-23-4	Tilton Bridge	3/10/77	9:00 A.M.
129-23-5	Calhoun Raw Water Intake	3/10/77	10:00 A.M.
129-23-6	Calhoun Finish Water	3/10/77	10:30 A.M.
129-23-7	Calhoun Filter Backwash	3/10/77	11:00 A.M.
129-23-8	Calhoun Waste Treatment Plant Influent	3/10/77	12:30 P.M.
129-23-9	Calhoun Waste Treatment Plant Effluent	3/10/77	12:50 P.M.
129-23-10	Oostananla Bridge at Ga. Highway 140	3/10/77	1:45 P.M.

TABLE 2

Concentration of Disperse Dyes (parts-per-billion) in Samples Taken from the Coosa River Basin

Sample	DR60	DR55	DY54	DY3	DY23	DB7	DB120
129-11-5	78	187	27	32	458	97	198
129-22-1	16	67	7	77	36	62	19
129-22-2	14	24	9	N.D.	17	35	17
129-22-3	N.D.	N.D.	N.D.	<1	<3	N.D.	N.D.
129-23-4	N.D.	N.D.	N.D.	<1	<3	N.D.	N.D.
129-23-5	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.
129-23-6	N.D.	N.D.	N.D.	<1	N.D.	N.D.	N.D.
129-23-7	N.D.	N.D.	N.D.	<1	N.D.	N.D.	N.D.
129-23-8	6	38	6	436	257	85	38
129-23-9	6	26	<2	17	10	152	37
129-23-10	N.D.	N.D.	N.D.	<1	N.D.	N.D.	N.D.

N.D. = not detected

Monthly Progress Report Number 23

June 1, 1977 - July 1, 1977

Survey of Coosa Basin for Organic Contaminants from Carpet Processing

Environmental Protection Division
Department of Natural Resources
State of Georgia

Prepared Under Contract No.
E-27-630

by

Wayne C. Tincher
School of Textile Engineering
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Atlanta, Georgia 30332

I. Introduction

A third sampling of the Coosa Basin was conducted this month and the collected samples prepared for analysis.

II. Third Sampling Trip

A third sampling trip was conducted on June 7 and 8. This time was selected to take advantage of the low flows experienced in early June. Samples were collected in the Rome area on June 7 and in the Dalton and Calhoun area on June 8. A listing of the samples collected is given in Table 1. The samples are numbered 129-30-1 through 129-32-5. Table 1 also includes samples previously collected so that all samples under analysis are given in Table 1. All samples were refrigerated immediately after collection and remained refrigerated until concentrated except finish water samples. Finish water samples were refrigerated within 8 hours of collection. Three mud samples were collected to determine the quantity of dyestuffs that may be absorbed on mud in the Coosa Basin. These samples will require a different extraction procedure as outlined below.

III. Sample Concentration

All water samples have been concentrated using the XAD-2 resin adsorption procedure previously described. A concentration factor of 180 (1800 ml → 10 ml) was achieved with these samples.

The mud samples were concentrated by placing 100 gram samples in a Sohxlet extractor and extracting with benzene, methanol and the pyridine-ammonium hydroxide-tetrahydrofuran mixture for 24 hours. The same

extracting solvent was used for subsequent 100 gram samples until a total of 1000 grams of mud had been extracted. The extracts were rotavapped to dryness and taken up in 10 ml of solvent.

Although this procedure has not been previously investigated, the extracts are highly colored suggesting that dye has been extracted from the mud samples.

IV. Future Work

Analysis of the sample concentrates by liquid chromatography will continue next month.

TABLE 1

Coosa Basin Samples Collected

Sample	Collection Site	Time of Collection	
129-10-2	Dalton Raw Water Intake	10/28/76	11:45 A.M.
129-11-5	Dalton Waste Treatment Plant Influent	10/28/76	3:15 P.M.
129-11-8	Dalton Waste Treatment Plant Effluent	10/28/76	4:15 P.M.
129-12-9	Looper's Bridge	10/28/76	5:15 P.M.
129-22-1	Dalton Waste Treatment Plant Influent	3/9/77	4:00 P.M.
129-22-2	Dalton Waste Treatment Plant Effluent	3/9/77	4:20 P.M.
129-22-3	Looper's Bridge	3/9/77	4:45 P.M.
129-23-4	Tilton Bridge	3/10/77	9:00 A.M.
129-23-5	Calhoun Raw Water Intake	3/10/77	10:00 A.M.
129-23-6	Calhoun Finish Water	3/10/77	10:30 A.M.
129-23-7	Calhoun Filter Backwash	3/10/77	11:00 A.M.
129-23-8	Calhoun Waste Treatment Plant Influent	3/10/77	12:30 P.M.
129-23-9	Calhoun Waste Treatment Plant Effluent	3/10/77	12:50 P.M.
129-23-10	Oostananla Bridge at Ga. Highway 140	3/10/77	1:45 P.M.
129-30-1	Rome Raw Water Intake	6/7/77	9:20 A.M.
129-30-2	Rome Finish Water	6/7/77	9:35 A.M.
129-30-3	Rome Waste Treatment Plant Influent	6/7/77	3:35 P.M.
129-30-4	Rome Waste Treatment Plant Effluent	6/7/77	9:00 P.M.
129-30-5	Looper's Bridge	6/7/77	5:45 P.M.
129-31-1	Looper's Bridge Mud Sample	6/7/77	6:00 P.M.
129-31-2	Tilton Bridge	6/8/77	10:35 A.M.
129-31-3	Tilton Bridge Mud Sample	6/8/77	10:55 A.M.

Table 1 (cont'd.)

Sample	Collection Site	Time of Collection
129-32-1	Calhoun Water Intake Mud Sample	6/8/77 11:30 A.M.
129-32-2	Calhoun Raw Water Intake	6/8/77 11:30 A.M.
129-32-3	Calhoun Finish Water	6/8/77 11:45 A.M.
129-32-4	Calhoun Waste Treatment Plant Influent	6/8/77 1:15 P.M.
129-32-5	Calhoun Waste Treatment Plant Effluent	6/8/77 1:30 P.M.

Monthly Progress Report Number 24

July 1, 1977 - Aug. 1, 1977

Survey of Coosa Basin for Organic Contaminants from Carpet Processing

Environmental Protection Division
Department of Natural Resources
State of Georgia

Prepared Under Contract No.
E-27-630

by

Wayne C. Tincher
School of Textile Engineering
Georgia Institute of Technology
Atlanta, Georgia 30332

I. Introduction

Major effort this month has been directed toward completion of the analysis of water and wastewater samples for disperse dyes.

II. Analysis for Samples Collected June 7 and 8

The samples collected last month at Dalton, Rome and Calhoun have been analyzed for the seven disperse dyes. All samples have been concentrated 180-fold (1800 ml→ 10 ml) by the resin adsorption procedure. With the concentration procedure and liquid chromatography separation and detection, the lower limit of quantitation is 1 part-per-billion for Disperse Yellow 3, Disperse Yellow 23, Disperse Yellow 54, Disperse Red 55 and Disperse Red 60. Disperse Blue 7 can be quantitated above 10 ppb and Disperse Blue 120 above 25 ppb. The blue dyes have a number of components which reduces the overall signal-to-noise ratio.

A list of samples is given in Table 1 for reference. The results of the analysis for disperse dyes is given in Table 2. A more careful analysis of the chromatograms has resulted in some minor changes in the data as reported in Progress Report Number 22.

The results for samples 129-30-3 (Influent to the Rome Wastewater Treatment Plant) and 129-30-4 (Effluent from the Rome Wastewater Treatment Plant) are interesting in that they suggest that the Rome plant is less effective in removing disperse dyes than the Calhoun and Dalton plants.

III. Future Work

Mud samples will be analyzed next reporting period.

TABLE 1

Coosa Basin Samples Collected

Sample	Collection Site	Time of Collection	
129- 10-2	Dalton Raw Water Intake	10/28/76	11:45 A.M.
129-11-5	Dalton Waste Treatment Plant Influent	10/28/76	3:15 P.M.
129-11-8	DaltonWaste Treatment Plant Effluent	10/28/76	4;15 P.M.
129-12-9	Looper's Bridge	10/28/76	5:15 P.M.
129-22-1	Dalton Waste Treatment Plant Influent	3/9/77	4:00 P.M.
129-22-2	Dalton Waste Treatment Plant Effluent	3/9/77	4:20 P.M.
129-22-3	Looper's Bridge	3/9/77	4:45 P.M.
129-23-4	Tilton Bridge	3/10/77	9:00 A.M.
129-23-5	Calhoun Raw Water Intake	3/10/77	10:00 A.M.
129-23-6	Calhoun Finish Water	3/10/77	10:30 A.M.
129-23-7	Calhoun Filter Backwash	3/10/77	11:00 A.M.
129-23-8	Calhoun Waste Treatment Plant Influent	3/10/77	12:30 P.M.
129-23-9	Calhoun Waste Treatment Plant Effluent	3/10/77	12:50 P.M.
129-23-10	Oostananla Bridge at Ga. Highway 140	3/10/77	1:45 P.M.
129-30-1	Rome Raw Water Intake	6/7/77	9:20 A.M.
129-30-2	Rome Finish Water	6/7/77	9:35 A.M.
129-30-3	Rome Waste Treatment Plant Influent	6/7/77	3:35 P.M.
129-30-4	Rome Waste Treatment Plant Effluent	6/7/77	9:00 P.M.
139-30-5	Looper's Bridge	6/7/77	5:45 P.M.

Table 1 (cont'd.)

Sample	Collection Site	Time of Collection	
129-31-1	Looper's Bridge Mud Sample	6/8/77	6:00 P.M.
129-31-2	Tilton Bridge	6/8/77	10:30 A.M.
129-31-3	Tilton Bridge Mud Sample	6/8/77	10:55 A.M.
129-32-1	Calhoun Water Intake Mud Sample	6/8/77	11:30 A.M.
129-32-2	Calhoun Raw Water Intake	6/8/77	11:30 A.M.
129-32-3	Calhoun Finish Water	6/8/77	11:45 A.M.
129-32-4	Calhoun Waste Treatment Plant Influent	6/8/77	1:15 P.M.
129-32-5	Calhoun Waste Treatment Plant Effluent	6/8/77	1:30 P.M.

TABLE 2

Concentration of Disperse Dyes (parts-per-billion) in Samples Taken from the Coosa River Basin

Sample	DY 3	DY 23	DY 54	DR 55	DR 60	DB 7	DB 120
129-10-2	-	-	-	-	-	-	-
129-11-5	32	458	27	187	78	97	198
129-22-1	77	36	7	67	16	62	< 25
129-22-2	+	17	9	24	14	35	< 25
129-22-3	< 1	3	+	-	+	-	-
129-23-4	< 1	3	+	+	-	-	-
129-23-5	-	-	-	-	-	-	-
129-23-6	< 1	-	-	-	-	-	-
129-23-7	< 1	-	-	-	+	-	-
129-23-8	436	257	6	38	6	85	38
129-23-9	17	10	2	26	6	152	37
129-23-10	< 1	-	-	-	+	-	-
129-30-1	< 1	+	-	-	-	-	-
129-30-2	-	-	-	-	-	-	-
129-30-3	222	93	13	4	52	19	57
129-30-4	256	120	32	11	76	26	114
129-30-5	3	2	5	3	-	22	<25
129-31-2	< 1	-	-	-	-	-	-
129-32-2	-	-	-	-	-	-	-
129-32-3	-	-	-	-	-	-	-
129-32-4	209	77	3	86	21	239	56
129-32-5	+	36	< 1	20	-	139	56

Monthly Progress Report Number 25

Aug. 1, 1977 - Sept. 1, 1977

Survey of Coosa Basin for Organic Contaminants from Carpet Processing

Environmental Protection Division
Department of Natural Resources
State of Georgia

Prepared Under Contract No.
E-27-630

by

Wayne Tincher
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Atlanta, Georgia 30332

I. Introduction

Major effort this month has been directed toward analysis of the mud samples in the Coosa Basin and set-up of new equipment for acid dye analysis.

II. Analysis of Mud Samples

During the June 7 and 8 sampling trip, mud samples were collected at the Looper's Bend Bridge, at the Tilton Bridge and near the intake of the Calhoun water treatment plant. One kilogram samples of the muds were extracted with benzene and with the methanol plus the pyridine-ammonium hydroxide-tetrahydrofuran solvent mixture. The extracts were rotavapped to dryness and taken up in either 50 or 25 ml of solvents for liquid chromatographic analysis. The concentration factor for samples 129-31-3 and 129-32-1 was 40 and for sample 129-31-1 the factor was 20.

Results of the analysis of the mud samples for disperse dyes is shown in Table 1. The mud samples show dye concentrations of the order of a few parts-per-million.

III. Acid Dye Analysis

The gradient program unit has been received from the manufacturer after a number of delays. A new 5 micron particle size reverse phase column has also been obtained which should permit greater resolution of the acid dyes. These instrument modifications are now being set up and evaluated.

IV. Future Work

Analyses of samples from the Dalton advanced waste treatment study will be reported next month.

TABLE 1

Analyses of Mud Samples

(parts-per-billion)

Sample No.	Site	DY 3	DY 23	DY 54	DR 55	DR 60	DB 7	DB 120
129-31-1	Looper's Bridge	420	2970	1600	-	3400	1405	3000
129-31-3	Tilton Bridge	455	1350	970	+	1050	625	3250
129-32-1	Calhoun Water Intake	140	114	31	119	19	-	62

\- dye not detected

\+ dye detected but below minimum concentration for quantitation

Monthly Progress Report Number 26

September 1, 1977 - October 1, 1977

Survey of Coosa Basin for Organic Contaminants from Carpet Processing

Environmental Protection Division
Department of Natural Resources
State of Georgia

Prepared Under Contract No.
E-27-630

by

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I. Introduction

Work this month has been directed toward analysis of samples collected as part of the Dalton Waste Treatment Plant Tertiary Treatment System study.

II. Samples

The dye analysis techniques developed at Georgia Tech have been used to evaluate the efficiencies of a number of tertiary treatment procedures for dye wastewater. The treatment systems were set-up at the Dalton Waste Treatment Plant and samples were collected as shown in Figure 1. All samples were 48 hour composites obtained in duplicate at seven locations in the processes. The samples were collected in 1 gallon glass containers and were refrigerated at $0^{o}C$ until concentrated in organic solvents. A list of the samples is given in Table 1.

III. Analysis for Disperse Dyes

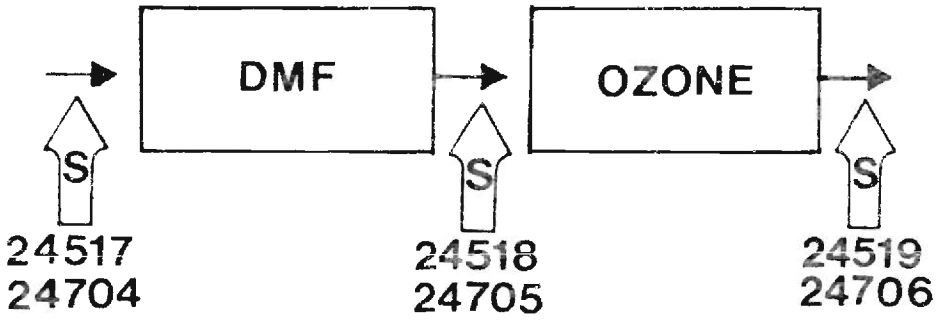
The wastewater samples were concentrated by macroreticular resin adsorption (XAD-2). The disperse dyes were removed from the column in benzene. The concentration factor was 180 (1800 ml waste concentrated in 10 ml benzene). The disperse dyes were separated on a cyanoethyl modified silica column and quantitated with a UV-visible spectrophotometer.

Results of the analyses are shown in Table 2. The levels of disperse dyes in these samples are somewhat lower than observed for previous analyses. Part of this difference is probably due to the nature of the samples. Previous samples were grab samples taken at the time of peak

carpet dyeing waste flow and should reflect maximum dye concentrations. These samples were composites taken over 48 hours. Although the dye levels are quite low, the results at least suggest that the tertiary treatment systems are not particularly effective in removing disperse dyes from wastewater.

IV. Future Work

Analyses of samples for acid dyes will be reported next month.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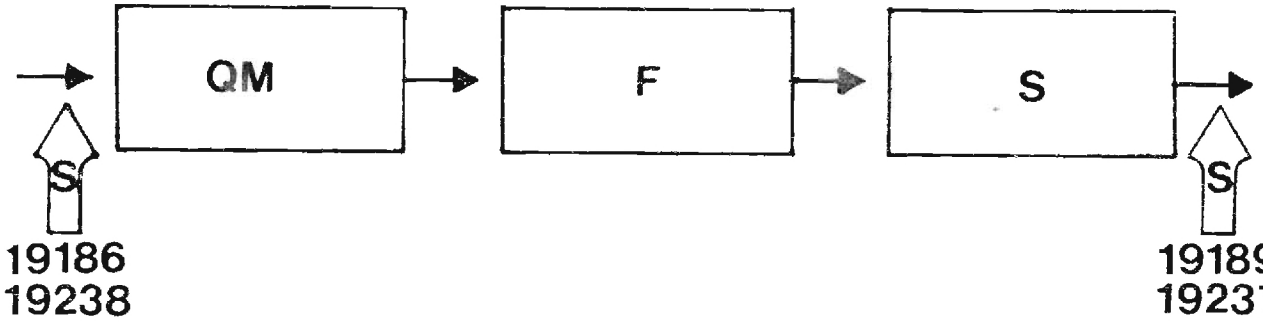
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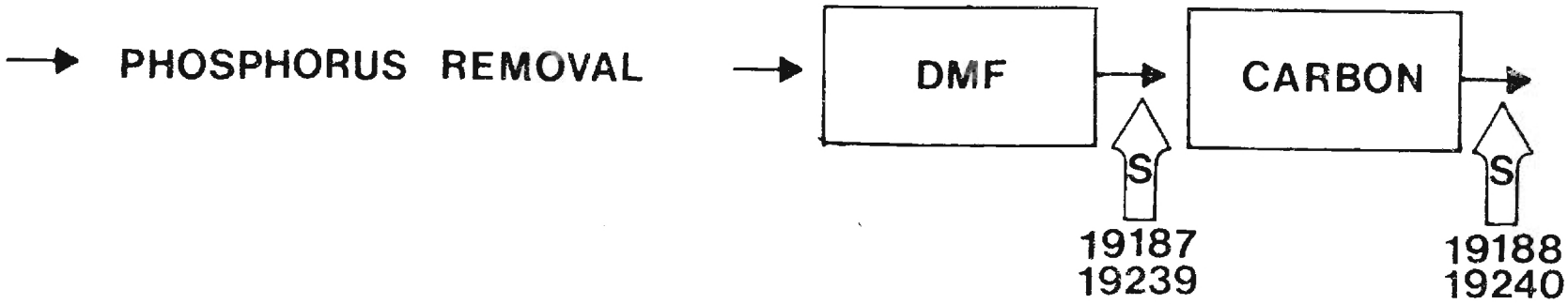
PHOSPHORUS REMOVAL
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19187
19239
19188
19240

Table 1

Samples for Dye Analysis

Sample	Location	Date
24517	Reactor Effluent	July 5-7
24518	Dual Media Filter Effluent	July 5-7
24519	Ozone Treatment Effluent	July 5-7
24704	Reactor Effluent	July 12-14
24705	Dual Media Filter Effluent	July 12-14
24706	Ozone Treatment Effluent	July 12-14
19186	Reactor Effluent	May 18-20
19189	Mixed Liquor Before P Removal	May 18-20
19187	Dual Midia Filter Effluent	May 18-20
19188	Activated Carbon Effluent	May 18-20
19238	Reactor Effluent	May 23-25
19237	Mixed Liquor Before P Removal	May 23-25
19239	Dual Media Filter Effluent	May 23-25
19240	Activated Carbon Effluent	May 23-25

Table 2

Disperse Dyes in Samples Collected in Dalton
Waste Treatment Plant Study

Sample	DY 3	DY 23	DY 54	DR 55	DR 60	DB 7	DB 120
19186	+	- *	1.8	3.0	5.5	+	-
19187	+	- *	1.3	3.0	2.3	+	-
19188	+	+	<1.0	+	+	-	-
19189	+	- *	+	+	+	-	-
19237	+	+	+	+	+	+	-
19238	+	2.2	+	-	+	+	-
19239	+	1.6	+	-	+	+	-
19240	1.9	2.8	+	-	+	-	-
24517	+	+	2.1	+	+	-	-
24518	+	+	1.1	+	+	-	-
24519	+	1.2	<1.0	-	1.7	-	-
24704	+	+	1.4	1.6	+	+	-
24705	+	- *	1.1	2.3	+	+	-
24706	+	1.8	- *	2.0	+	-	-
lower limit for quantitation	1 ppb	1 ppb	1 ppb	1 ppb	1 ppb	10 ppb	25 ppb

\+ dye detected but concentration much less than 1 ppb

\- dye not detected

* dye may be present in very low concentration but interference by an impurity prevents quantitation.

Monthly Progress Report Number 27

October 1, 1977 - November 1, 1977

Survey of Coosa Basin for Organic Contaminants from Carpet Processing

Environmental Protection Division
Department of Natural Resources
State of Georgia

Prepared Under Contract No.
E-27-630

by

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I. Introduction

Major effort this month has been directed towards analysis of the samples from the Dalton Waste Treatment Plant Tertiary Treatment System Study for acid dyes.

II. Analysis for Acid Dyes

The wastewater samples were concentrated by macroreticular resin adsorption and the acid dyes removed from the column by backwashing with methanol and a tetrahydrofuran-pyridine-ammonium hydroxide solvent mixture. The extracts were combined, rotavapped to dryness and taken up in 10 ml of methanol. The overall concentration factor was 180.

The dye concentrates were separated by liquid chromatography on a hydrocarbon modified column using the paired ion technique. Detection and quantitation were achieved using a UV-visible spectrophotometer.

A list of the samples analyzed is given in Table 1 for reference. Results of the analysis for acid dyes are given in Table 2.

III. Discussion

The results of the analysis for acid dyes yields much more information about the waste treatment systems than the disperse dye analyses. First, the overall levels of acid dyes are much higher in the effluents. The data for yellow dyes (AY19, AY151, AY135) confirm previous results which suggest that Acid Yellow 19 and Acid Yellow 151 are significantly reduced by activated sludge treatment of dye wastes. Acid reds are not reduced as much. Second, the results suggest that ozone and carbon adsorption are very effective in removing acid dyes from the waste stream. Dual media filtration, on the other hand, is not effective for acid dyes.

IV. Future Work

Reports on acid dye analysis of other Coosa basin samples will be reported next month.

Table 1

Samples for Dye Analysis

Sample	Location	Date
24517	Reactor Effluent	July 5-7
24518	Dual Media Filter Effluent	July 5-7
24519	Ozone Treatment Effluent	July 5-7
24704	Reactor Effluent	July 12-14
24705	Dual Media Filter Effluent	July 12-14
24706	Ozone Treatment Effluent	July 12-14
19186	Reactor Effluent	May 18-20
19189	Mixed Liquor Before P Removal	May 18-20
19187	Dual Midia Filter Effluent	May 18-20
19188	Activated Carbon Effluent	May 18-20
19238	Reactor Effluent	May 23-25
19237	Mixed Liquor Before P Removal	May 23-25
19239	Dual Media Filter Effluent	May 23-25
19240	Activated Carbon Effluent	May 23-25

Table 2

Sample	AY19	AY151	AY135	A0128	AR337	AR151	AB40	AB25
24517	+	-	-	+	263	+	33	116
24518	-	18.7	-	+	268	+	47	107
24519	285.0	-	-	+	104	-	15	46
24704	-	-	-	56	541	4	174	209
24705	-	-	-	28	443	-	178	186
24706	+	-	-	-	-	-	-	-
19186	302	19	-	13	49	4	32	88
19189	-	63	8	+	21	5	8	17
19187	+	9	-	+	14	+	54	214
19188	+	-	-	-	+	-	+	7
19238	-	-	-	+	499	4	44	182
19237	+	32.3	-	14	19	11	18	33
19239	+	+	-	+	427	2	54	144
19240	-	-	-	-	+	2	14	11

+ dye detected but concentration less than 1 ppb

- dye not detected

Monthly Progress Report Number 28

November 1, 1977 - December 1, 1977

Survey of Coosa Basin for Organic Contaminants from Carpet Processing

Environmental Protection Division
Department of Natural Resources
State of Georgia

Prepared Under Contract No.
E-27-630

by

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I. Introduction

Analysis of all Coosa Basin samples (except mud samples) for acid dyes has been completed this month.

II. Analysis for Acid Dyes

The wastewater samples were concentrated by macroreticular resin adsorption and the acid dyes removed from the column by backwashing with methanol and a tetrahydrofuran-pyridine-ammonium hydroxide solvent mixture. The extracts were combined, rotavapped to dryness and taken up in 10 ml of methanol. The overall concentration factor was 180.

The dye concentrates were separated by liquid chromatography on a hydrocarbon modified column using the paired ion technique. Detection and quantitation were achieved using a UV-visible spectrophotometer. A linear solvent gradient (60/40 methanol/water to 85/15 methanol/water) was used to separate the acid dyes.

The samples analyzed are identified in Table 1 and the results of the analysis is given in Table 2.

Levels of acid dyes in the Coosa Basin samples are much higher than disperse dye levels. This probably reflects the fact that disperse dyes are removed by adsorption on the sludge in typical waste treatment plants and the acid dyes are not. Most samples contain all the acid dyes except Acid Yellow 135 and Acid Orange 108. The low levels of Acid Yellow 135 were not expected and may indicate some problem with the analytical system used. This possibility will be investigated. Acid Orange 108 is not used as extensively as the other acid dyes.

III. Future Work

Analysis of mud samples for acid dyes will be reported next month.

TABLE 1

Coosa Basin Samples Collected

Sample	Collection Site	Time of Collection	
129- 10-2	Dalton Raw Water Intake	10/28/76	11:45 A.M.
129-11-5	Dalton Waste Treatment Plant Influent	10/28/76	3:15 P.M.
129-11-8	DaltonWaste Treatment Plant Effluent	10/28/76	4:15 P.M.
129-12-9	Looper's Bridge	10/28/76	5:15 P.M.
129-22-1	Dalton Waste Treatment Plant Influent	3/9/77	4:00 P.M.
129-22-2	Dalton Waste Treatment Plant Effluent	3/9/77	4:20 P.M.
129-22-3	Looper's Bridge	3/9/77	4:45 P.M.
129-23-4	Tilton Bridge	3/10/77	9:00 A.M.
129-23-5	Calhoun Raw Water Intake	3/10/77	10:00 A.M.
129-23-6	Calhoun Finish Water	3/10/77	10:30 A.M.
129-23-7	Calhoun Filter Backwash	3/10/77	11:00 A.M.
129-23-8	Calhoun Waste Treatment Plant Influent	3/10/77	12:30 P.M.
129-23-9	Calhoun Waste Treatment Plant Effluent	3/10/77	12:50 P.M.
129-23-10	Oostananla Bridge at Ga. Highway 140	3/10/77	1:45 P.M.
129-30-1	Rome Raw Water Intake	6/7/77	9:20 A.M.
129-30-2	Rome Finish Water	6/7/77	9:35 A.M.
129-30-3	Rome Waste Treatment Plant Influent	6/7/77	3:35 P.M.
129-30-4	Rome Waste Treatment Plant Effluent	6/7/77	9:00 P.M.
139-30-5	Looper's Bridge	6/7/77	5:45 P.M.

Table 1 (cont'd.)

Sample	Collection Site	Time of Collection	
129-31-1	Looper's Bridge Mud Sample	6/8/77	6:00 P.M.
129-31-2	Tilton Bridge	6/8/77	10:30 A.M.
129-31-3	Tilton Bridge Mud Sample	6/8/77	10:55 A.M.
129-32-1	Calhoun Water Intake Mud Sample	6/8/77	11:30 A.M.
129-32-2	Calhoun Raw Water Intake	6/8/77	11:30 A.M.
129-32-3	Calhoun Finish Water	6/8/77	11:45 A.M.
129-32-4	Calhoun Waste Treatment Plant Influent	6/8/77	1:15 P.M.
129-32-5	Calhoun Waste Treatment Plant Effluent	6/8/77	1:30 P.M.

TABLE 2

Acid Dye Concentrations (in ppb) in
Coosa Basin Samples

Sample	AY-19	AY-151	AY-135	AB-40	AB-25	AR-337	AD-108	AR-151
129-10-2	-	-	-	-	-	-	-	-
129-11-5	1442.2	+	-	57.8	53.3	101.1	41.1	6.7
129-11-8	377.8	+	-	-	11.1	190.3	16.7	8.3
129-12-9	155.6	+	-	-	-	26.4	-	1.9
129-22-1	1199.4	1111.11	-	113.9	145.0	-	-	62.2
129-22-2	617.2	104.4	-	351.7	254.4	1019.4	+	77.2
129-22-3	+	7.8	-	21.1	16.1	41.7	-	8.3
129-23-4	62.2	-	-	29.4	15.0	42.2	-	2.5
129-23-5	37.8	-	-	-	-	8.3	-	1
129-23-6	-	-	-	-	-	-	-	-
129-23-7	-	-	-	-	-	-	-	-
129-23-8	126.7	57.2	+	252.8	53.9	55.6	137.2	6.7
129-23-9	211.7	132.2	+	403.3	73.9	27.8	268.9	75.6
129-23-10	-	-	-	-	-	+	-	+
129-30-1	10	-	-	-	-	-	-	-
129-30-2	-	-	-	-	-	-	-	-
129-30-3	22.8	134.4	-	+	18.9	69.4	48.9	4.6
129-30-4	301.1	3750.0	-	22.2	502.2	78.3	1116.1	48.3
129-30-5	8.9	+	-	7.2	41.7	88.9	15.0	1.4
129-31-2	171.7	+	-	+	14.4	18.9	-	-
129-32-2	31.7	-	+	-	-	5.2	-	-
129-32-3	-	3.8	-	-	+	-	-	-
129-32-4	98.9	118.9	12.6	86.7	32.2	13.3	-	-
129-32-5	171.7	-	-	196.7	27.2	-	+	-

Monthly Progress Report Number 29

December 1, 1977 - January 1, 1978

Survey of Coosa Basin for Organic Contaminants from Carpet Processing

Environmental Protection Division
Department of Natural Resources
State of Georgia

Prepared Under Contract No.
E-27-630

by

Wayne C. Tincher
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Atlanta, Georgia 30332

I. Introduction

Major effort this month has been directed toward analysis of mud samples collected in the Coosa Basin for acid dyes.

II. Analysis of Mud Samples

During the June 7 and 8 sampling trip, mud samples were collected at the Looper's Bend Bridge, at the Tilton Bridge and near the intake of the Calhoun water treatment plant. One kilogram samples of the muds were extracted with benzene and with the methanol plus the pyridine-ammonium hydroxide-tetrahydrofuran solvent mixture. The extracts were rotavapped to dryness and taken up in either 50 or 25 ml of solvents for liquid chromatographic analysis. The concentration factor for samples 129-31-3 and 129-32-1 was 40 and for sample 129-31-1 the factor was 20.

Results of the analysis of the mud samples for acid dyes is shown in Table 1. The mud samples show dye concentrations of the order of a few parts-per-million.

III. Future Work

This report completes the experimental work on Project E-27-630. A final report on the project is in preparation.

TABLE 1

Analysis of Mud Samples for Acid Dyes

Sample No.	Site	AY-19	AY-151	AY-135	AB-40	AB-25	AR-337	AD-128	AR-151
129-31-1	Looper's Bridge	2080	515	+	225	550	205	790	27
129-31-3	Tilton Bridge	1168	1105	+	113	315	173	615	35
129-32-1	Calhoun Water Intake	110	165	-	-	+	-	-	15

- dye not detected

+ dye detected not below minimum concentration for quantitation

E-27-630

Final Report

Survey of the Coosa Basin for Organic Contaminants from Carpet Processing

by

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Prepared Under Contract No.

E-27-630

for

Environmental Protection Division
Department of Natural Resources
State of Georgia

The preparation of this report was financed in part through a grant from the U.S. Environmental Protection Agency under provision of Section 116 of The Federal Water Pollution Control Act Amendments of 1972.

October, 1978

Final Report

Survey of the Coosa Basin for Organic Contaminants from Carpet Processing

by

Wayne C. Tincher
School of Textile Engineering
Georgia Institute of Technology
Atlanta, Georgia 30332

Prepared Under Contract No.

E-27-630

for

Environmental Protection Division
Department of Natural Resources
State of Georgia

The preparation of this report was financed in part through a grant from the U.S. Environmental Protection Agency under provision of Section 116 of The Federal Water Pollution Control Act Amendments of 1972.

October, 1978

Abstract

An analytical system has been developed for determination of the concentrations of 15 acid and disperse dyes in textile dyeing wastewaters. The dyes are removed from wastewater by adsorption on macroreticular resins (XAD-2) and recovered from the resin by backwashing with selected solvents. An increase in dye concentration of up to 180-fold can be achieved by the resin adsorption technique. Selection of backwashing solvents also permits quantitative separation of acid dyes from disperse dyes.

Dye mixtures were separated by liquid chromatography and the quantities of each of the 15 dyes present determined by absorption spectrophotometry. Thirteen of the dyes (DY 3, DY 23, DY 54, DR 60, DR 55, AY 151, AY 19, AY 135, AO 128, AR 537, AR 151, AB 25, AB 40) can be detected at 1 part-per-billion in wastewater. The other two dyes must be present at higher concentrations (DB 7 10 ppb and DB 120 25 ppb) to be detected.

The analytical system has been used to analyze 27 samples collected in the Coosa River basin for acid and disperse dyes. The results suggest that acid dyes are present in higher concentration than disperse dyes. City water supplies in the Coosa basin are relatively free from dye contamination. Mud samples in the Coosa basin do contain appreciable quantity of both acid and disperse dyes.

The analytical procedure has also been used to evaluate the effectiveness of biological and advanced waste treatment systems for removal of acid and disperse dyes. The results show that biological treatment is effective in removal of disperse dyes (probably by adsorption on sludge) but less

effective in acid dye removal. Ozone and carbon adsorption are effective in removal of acid dyes from wastewater.

Some further improvements to the analytical system are described and preliminary work to extend the system to analysis of direct dyes in wastewater is presented.

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I. Introduction

The carpet industry uses and discharges approximately 20 billion gallons of water annually [1]. This is of the order of 14 gallons of water per pound of carpet produced [2]. Over 50% of the total or 7 billion gallons of water is discharged each year to the Coosa River basin [3,4]. Data on the carpet industry in Georgia is shown in Table 1.

Most of the water used in carpet manufacturing is used in the dyeing process. Carpet dyeing and rinse water contains substantial quantities of dissolved and suspended organic and inorganic compounds. Since the Coosa River and its tributaries serve as a source of water for a number of cities and towns, the presence of these compounds in carpet wastewater is of considerable concern to officials responsible for water quality in the states of Georgia and Alabama.

A previous study [5,6] has indicated that carpet dyeing and finishing wastes may be classified in five major groups. These groups and the approximate quantities of each type discharged annually by the carpet industry are:

Inorganic compounds--13 million pounds
Volatile organic compounds-- 40 million pounds
Dyes --0.3 million pounds
Surfactants --16 million pounds
Other organic compounds --12 million pounds

Although dyes constitute a small portion of the total amount of waste discharged in carpet processing, this group is very important for several reasons. First, analytical procedures for the determination of individual dyes in complex mixtures are not available. Procedures for inorganic

Table 1

Distribution of the Georgia Carpet Industry
(SIC CODE 227)

Area	No. of Plants	Value of Shipments (Million Dollars)	%
United States (Total)	-	2,937	100.00
State of Georgia	248	1,727	58.8
Whitfield County	128	738	25.1
Gordon County	36	175	6.0
Bartow County	21	147	5.0
Murray County	19	36	1.2
Gilmer County	5	21	0.7
Eight Northwest Georgia Counties +*	-	1,499	51.0

+ Whitfield, Bartow, Catoosa, Chattooga, Floyd, Gordon, Murray, Walker.

* Data from Georgia Economic Model which may be on slightly different basis than other data in the table [6].

compounds [7], for volatile organic compounds [8], and for surfactants [9] in wastewater are generally available. Extensive work on the analytical chemistry of dyes [10] has been reported in the literature but no analytical system has been developed for determination of dyes at the fractional parts-per-million level in the complex mixtures typically encounted in waste streams.

Second, dyes in textile waste streams are important because they are not readily removed by typical waste treatment processes. Most textile wastes receive some type of biological oxidation (lagoon, oxidation pond, trickling filter, activated sludge) prior to discharge to streams and rivers. Although biological treatment is effective in reduction of biochemical oxygen demand, it is not effective in color reduction. For example, in a joint Environmental Protection Agency - American Dye Manufacturers Institute study of 9 dyes [11], laboratory biological treatment removed from 42% to 97% of the color when the dyes were added to domestic waste and treated. Only 1 acid and 1 disperse dye were used in this study and both showed less than 50% removal. Removal of color from 30% [12] to 68% [13] has been reported for activated sludge treatment plants with substantial textile dye wastewater in the influent. These data clearly demonstrate the resistance of dyes to treatment techniques currently employed.

Third, the possible long term health effects of dyes and dye degradation products are becoming of increasing concern. The possible mutagenic, carcinogenic, and/or teratogenic effects of dyes are now under investigation in a number of laboratories [14-16]. The preliminary results from this work suggest that analysis for specific dyes may be important in identifying and quantifying possible health hazards.

In addition to quantitative determination of dyes in wastewater and in streams and rivers, an analysis system for dyes is important for evaluation of the effiencie y of dye removal by both current and new treatment systems. Thus, the work was undertaken to develop an analytical system to determine the concentration of dyes commonly used in carpet processing.

The work is divided into four parts. Part I describes the analytical procedures developed for acid and disperse dyes, Part II describes the use of these procedures for analysis of samples collected in the Coosa River basin, Part III details the use of the system for evaluating advanced treatment systems for dye removal efficiencies, and Part IV describes the extension of the analytical system to direct dyes.

Part I

Development of Analytical Procedures for Dyes in Wastewater

A. Objective and Approach

The objective of the first phase of the project was the development of an analytical system for determination of the concentrations of acid and disperse dyes in wastewater at the parts-per-billion level. Based on the previous studies of chemical use in the carpet industry [5], it was estimated that dyes would be present in carpet processing wastes at the fractional parts-per-million level. Analytical techniques for dyes (visible absorption spectroscopy) can readily detect dyes at the parts-per-million level. An approximate 100-fold concentration procedure was necessary, therefore, to obtain dyes at a concentration suitable for quantitative analysis. Since dyes always occur in mixtures in wastewater, a separation procedure was also required. The most distinctive characteristic of dyes is their very strong absorption of energy in the visible region of the spectrum. This characteristic was selected for development of a method for quantitation of the concentrated and separated dyes.

B. Dyes Selected for Study

Two major classes of dyes - acid dyes and disperse dyes - and a few basic and direct dyes are used in carpet piece dyeing. Fifteen dyes from the acid and disperse classes were selected for study. These dyes are shown in Table 2. These 15 dyes account for over 50% of all the dyes used in carpet piece dyeing [5]. The dyes from this group whose structures are known are shown in Appendix A.

Table 2

Dyes Selected for Development
of Analytical Techniques

Acid Yellow 19	Disperse Blue 7
Acid Yellow 135	Disperse Blue 120
Acid Yellow 151	Disperse Yellow 3
Acid Orange 128	Disperse Yellow 23
Acid Red 151	Disperse Yellow 54
Acid Red 337	Disperse Red 55
Acid Blue 25	Disperse Red 60
Acid Blue 40	

C. Preparation of Dye Standards

Dyes as sold by dyestuff manufacturers contain many materials in addition to the dye component. Commercial disperse dyes usually contain from 15 to 30% dye and commercial acid dyes are generally of the order of 50% pure [5]. Materials present in commercial dyes in addition to the dye include dispersing agents, salt, sugar, sodium sulfate, and other additives and diluents. For the purposes of this study it was necessary to prepare samples of pure dye to use as analytical standards.

Disperse dyes were purified by Soxhlet extraction with benzene. Approximately 50 grams of dye were placed in a glass extraction thimble and extracted with benzene for 12 hours. The dye is soluble in benzene but the more polar diluents and dispersing agents are insoluble. The dye was recovered by removal of the benzene in a rotary evaporator. The recovered dye was again extracted with benzene and the process repeated until the extinction coefficient of the dye reached a constant value. This usually occurred after three extraction and recovery cycles.

Acid dyes were purified by recrystallization from methanol. Approximately 50 grams of dye were dissolved in 500 milliliters of methanol. The acid dyes are readily soluble in methanol but the inorganic salts present in the commercial dye are insoluble. The solution was filtered and the dye recrystallized from the filtrate. This procedure was also repeated until the dye extinction coefficient reached a constant value. This also generally required about three cycles.

Standard solutions were prepared by weighing out 1.00000 grams of dye on a Mettler Microanalytical Balance (capable of weighing to 0.000001 grams).

The dye was transferred to a 1 liter volumetric flask and solvent added to give 1 liter of solution.

Some difficulty was encountered in dissolving the pure disperse dyes in benzene, the selected solvent. With no dispersing agent present the dye was difficult to dissolve completely. This problem was solved by pasting the dye with dimethylformamide and then adding the benzene. Thus the standard disperse dye solution contained the dye dissolved in a 1% dimethylformamide (DMF), 99% benzene solvent. Similarly, the standard acid dye solutions were prepared in 1% DMF, 99% methanol solvent.

Solutions containing 5, 10, and 20 parts-per-million (ppm) of the pure dyes in solution were prepared by dilution of the standard 1 gram per liter solution with 1% DMF in either methanol or benzene.

D. Concentration Procedures

The necessity for an approximately 100-fold increase in dye concentration suggested that some type of adsorption procedure would be most convenient for the concentration step. Previous work [6,17-20] on a number of possible adsorbants had shown that macroreticular resins were promising for removal of dyes from solution. These resins are copolymers of styrene with divinylbenzene and have a high surface-to-volume ratio. Of the available resins Amberlite XAD-2 (Rohm and Haas Company) was found to give the best removal and recovery of dyes from wastewater. Further work, therefore, was concentrated on development of a recovery and concentration procedure based on XAD-2 resin adsorption.

One problem with adsorption of disperse dyes arises due to the fact that these dyes are not molecularly dispersed in water. They are, therefore,

not efficiently removed by adsorption processes. During the course of this work it was discovered that the addition of 10% DMF to water dispersion of disperse dyes would greatly increase the recovery of the dye from the water.

1. Column Preparation

Lab-Crest 9 mm by 500 mm chromatography columns equipped with demountable Teflon stopcocks were used for column preparation. Amberlite XAD-2 resin (30 ml) was slurred in approximately 60 ml of methanol and run through the column as rapidly as possible ($\sim$ 5 minutes). A glass wool plug was used in the bottom of the column to return the resin. The column was then washed with 40 ml of benzene at approximately 2 bed volumes per hour. The benzene wash was followed by a 40 ml methanol upflow wash at 8 bed volumes per hour to reclassify the column and to remove air bubbles resulting from the benzene wash. The column was then washed with 40 ml of each solvent used in the extraction of dye from the resin to ensure that any impurities likely to come off the column with the dyes would be removed. The column was given a final wash with 200 ml of distilled water and stored under distilled water until used. Column preparation and use procedures have been described in detail in Rohm and Haas Technical Bulletins [17,21].

2. Recovery Studies

In preliminary development of the recovery system, 200 ml of a 1 ppm dye solution in 10% DMF and 90% water were passed through the column at 8 bed volumes per hour (approximately 350 ml/hour).

The column was then washed with 50 ml of 10% DMF and 90% water, the column inverted and back washed with selected solvents to remove the dyes. The removed dyes were taken up in a known volume of solvent and the dye concentration determined spectrophotometrically. The percent recovery of the dye could thus be determined from the known quantity of dye in the original solution and the amount recovered from the column by the back-washing procedure.

A number of experimental parameters were studied to establish details of the concentration procedure. The effect of column diameter was investigated using 9 mm and 15 mm columns. The results indicated that column diameter did not influence the recovery. Subsequent studies were carried out on the smaller columns to reduce the volume of recovery solvents required. Resin bed depths of 25 and 40 cm were studied also. Recoveries of dyes were slightly better at 40 cm so the larger bed depths were used in further studies.

Solvents used in recovery had a major affect on recovery efficiencies. Early studies showed that benzene readily removes disperse dyes from the resin column. Recoveries were better than 70% for each of the seven disperse dyes investigated. Recovery of acid dyes proved more difficult. A number of solvents including, DMF, methanol, tetrahydrofuran, pyridine and ammonia were tried. The system that gave best results involved back-washing with two solvent systems. The acid dyes were removed by first eluting with 40 ml of methanol followed by 40 ml of a pyridine, tetrahydrofuran, 1% ammonium hydroxide (40:40:20) solvent mixture, both at a rate of 4 bed volumes per hour. This elution system gave better than 70% recovery of each of the acid dyes.

3. Concentration system.

The final system developed for concentration of the dyes required the following steps. Columns were prepared as described previously. A 1000 ml Kelly infusion jar was attached to the top of the resin column with a 1 inch piece of silicone tubing of 0.1925 inches I.D. (Cole-Palmer). Wastewater (900 ml) and dimethylformamide (100 ml) were placed in the Kelly influsion jar and allowed to flow down the column at 4 bed volumes (120 ml) per hour. As indicated earlier, the dimethylformamide is added to increase the solubility of disperse dyes so that they will be adsorbed by the resin. If dye is present in the wastewater, colored bands will appear near the top of the column. After all the wastewater has passed through the column, the reservoir and column were washed with 50 ml of a 90% water- 10% dimethyl-formamide mixture to insure that all of the wastewater sample had contacted the column.

Since the dye is concentrated near the top of the column, the reservoir and stopcocks were removed and the column inverted for the subsequent elution steps. A 9 mm x 500 mm extension column was attached to the top to serve as a solvent reservoir. The column was first eluted with 40 ml benzene at approximately 2 bed volumes per hour. The disperse dyes are removed by benzene and the acid dyes remain on the column. The acid dyes were removed by first eluting with 40 ml of methanol followed by 40 ml of the pyridine, tetrahydrofuran, 1% ammonium hydroxide (40:40:20) mixture, both at a rate of 4 bed volumes per hour.

The benzene containing the disperse dyes was collected in a 50 ml round bottom flask equipped with a 24/40 ground glass joint. The flask was placed on a Buchi Rotavap R and benzene removed under aspirator vacuum at temperatures up to 100°C. The disperse dyes were taken up in a 1% dimethylformamide - 99% benzene solvent and made up to 10, 25 or 50 ml in a volumetric flask depending on the desired increase in concentration.

The methanol and solvent mixture extracts were combined in a 250 ml round bottom flask and rotavapped as described above for the benzene extracts. The residual acid dyes were taken up in 1% dimethylformamide - 99% methanol and made up to the desired volume.

The recovery efficiencies for 1 part-per-million solutions of the 15 important carpet dyes using the above procedure are shown in Table 3.

The concentration procedure was generally used to concentrate the dyes in 900 ml of wastewater in a volume of 10 ml for an overall concentration factor of 90. In some cases 2 columns were used and 900 ml of wastewater run through each column. Combining the eluents from the two columns gave a concentration factor of 180.

In addition to concentration of the dyes, the resin adsorption procedure also provided a separation of the acid and disperse classes of dyes. This separation was quantitative and greatly simplified the subsequent analytical procedures. The separated and concentrated acid and disperse dyes were now ready for the separation and quantitation procedure.

E. Separation and Quantitation

Dye mixtures have traditionally been separated by thin-layer chromatography. In previous work [6] on the 7 disperse dyes and 8 acid dyes

Table 3

Recovery of Carpet Dyes From Wastewater
By Resin Adsorption

Acid Dyes		Disperse Dyes	
Acid Yellow 151	75%	Disperse Yellow 23	77%
Acid Red 337	75%	Disperse Yellow 3	98%
Acid Yellow 19	70%	Disperse Yellow 54	77%
Acid Yellow 135	100%	Disperse Red 60	89%
Acid Orange 128	76%	Disperse Red 55	95%
Acid Red 151	97%	Disperse Blue 7	73%
Acid Blue 25	80%	Disperse Blue 120	83%
Acid Blue 40	84%		

under investigation in this study it had been demonstrated that thin-layer chromatography could be used to separate both the acid and disperse dyes. This technique however, is difficult, does not lend itself to quantitative analysis, and is not readily adaptable to analyses of large numbers of routine samples.

Recent developments in technology have made rapid and quantitative separation of complex mixtures possible by high pressure liquid chromatography (HPLC). In this technique, components to be separated are dissolved in a suitable solvent and pumped onto a column containing a small particle, high surface area adsorbant. The differing partition of the various components between the stationary phase and the moving solvent phase results in a separation of the components as they move down the column. The instrument may be operated in a variety of modes depending on the nature of the stationary phase. In the case of small particle silica columns, a type of adsorption chromatography is responsible for the separation. In other cases a liquid-like hydrocarbon (e.g., C_{18} chains) are adsorbed on or bonded to the column and a type of liquid-liquid partition is achieved. Ionic species may also be bonded to the column for separation of polar components. Columns containing specific pore sizes are available to obtain separations based on molecular size (exclusion chromatography). This range in operation mode combined with the variety of solvents and solvent mixtures which may be used as mobile phases provides an extremely versatile separation tool. Detection of components exiting from the column is usually achieved by adsorption in the UV and/or visible spectrum. Thus, the detector systems are especially sensitive to dye molecules and the aromatic portions of many

surfactant molecules. By operating in the visible region of the spectrum dyes can be detected and quantitated in the presence of the many other organic compounds in dye wastewater which do not absorb strongly in the visible region. Similarly, selection of absorbing wavelength makes possible determination of, for example, yellow dyes even when blue dyes elute at the same retention time. Thus wavelength selection can greatly simplify the separation process.

HPLC has been applied to the separation of both azo and anthraquinone dyes by a variety of techniques in a number of recent papers. An excellent review of this work had been presented by Papa [10]. HPLC was selected, therefore, as the method for separation and quantitation of the dyes selected for study in this work.

1. Equipment

Two different liquid chromatographs were used during the course of the work. Early development work was carried out on a Micromeritics Model 7000 HPLC. This instrument can be operated in either an isocratic (fixed solvent composition) or gradient (time variant solvent composition) mode. It is equipped with a variable wavelength UV-visible detector. The only difficulty encountered with this instrument was in analyses for blue dyes. The output of the detector light source was very low at wavelengths above 600 nm. It was not possible to detect blue dyes at low concentration.

Most of the later work employed a HPLC system assembled from components. This system had a Laboratory Data Control Pumping System (Constametric I and II pumps with a Constametric II G Control Module and Model 7120 Gradient

Master), a Rheodyne Model 7120 Syringe Loading Sample Injector, a Tracor Model 970 Variable Wavelength Absorbance Detector, and a Houston Instrument Omniscribe Recorder with a built-in integrator. This instrument system performed very well in all dye analyses.

2. Analysis for Disperse Dyes

a. Column and Solvent Selection

The structure and polarity of disperse dyes suggested that absorption liquid chromatography would be the best technique for separation. In this technique, compounds are adsorbed on a polar surface and separations are achieved based on differences in polarity of components. Initially, a small particle 10μ silica column was investigated for separation of disperse dyes. The disperse dyes were so strongly adsorbed on this column that they were very difficult to remove with even the most polar solvents.

Best separation of the disperse dyes was obtained with a column of intermediate polarity. The column employed was a 25 cm Partisil-10 PAC column (Whatman) which has cyanoethyl groups bonded to a 10μ irregular silica substrate.

A solvent system consisting of a nonpolar component (nonsolvent) and a polar component (solvent) is generally used in adsorption chromatography as the mobile phase. Several polar compounds--tetrahydrofuran, dioxane, isopropyl alcohol, methyl alcohol, dimethylformamide--which are solvents for disperse dyes were considered for the strong solvent. Isooctane, cyclohexane,

benzene, carbon tetrachloride and heptane were employed as weak or nonpolar solvents. Disperse Blue 7 was the disperse dye most strongly adsorbed by the PAC column. It was useful for screening candidate solvents since the mobile phase must be capable of eluting the strongest held solute from the column in a reasonble time. After study of a large number of solvent-nonsolvent pairs, tetrahydrofuran (THF) and cyclohexane (CH) were selected for separating the disperse dyes.

Elution volumes in ml for the disperse dyes on Partisil PAC with a number of tetrahydrofuran-cyclohexane mixtures are shown in Table 4. There is some scatter in the data due to failure of the solvent mixing valve during a few of the runs. The results suggest that a solvent-nonsolvent gradient beginning at a ratio of 25/75 THF/CH and increasing to 100% THF should give good separation of the 7 disperse dyes. This gradient system gave excellent separation of the disperse yellow dyes as can be seen in Figure 1.

Difficulties were encountered in using the gradient system for the disperse red and disperse blue dyes. These dyes are not single compounds and the gradient system separated each of these dyes into a number of components. This problem is illustrated in Figure 2 where at least 6 components are observed for Disperse Blue 7. This separation greatly reduces the signal-to-noise ratio and decreases the sensitivity of the analytical method. Specific solvent ratios were therefore used

Table 4

Elution Volumes (ml) for Disperse Dyes on Partisil PAC

	25/75	30/70	35/65	40/60	50/50	60/40	75/25	80/20	81/19	90/10
DB 120	7.0	8.8	4.9	6.4	3.8		3.5			
DR 60	5.1		4.3		3.6	4.3				
DY 54	6.1		4.9		3.9					
DY 23	10.2		7.8		4.8				3.4	
DB 7								14.9		10.9
DR 55				4.0	9.4	5.2				
DY 3					15.7			3.6	4.9	

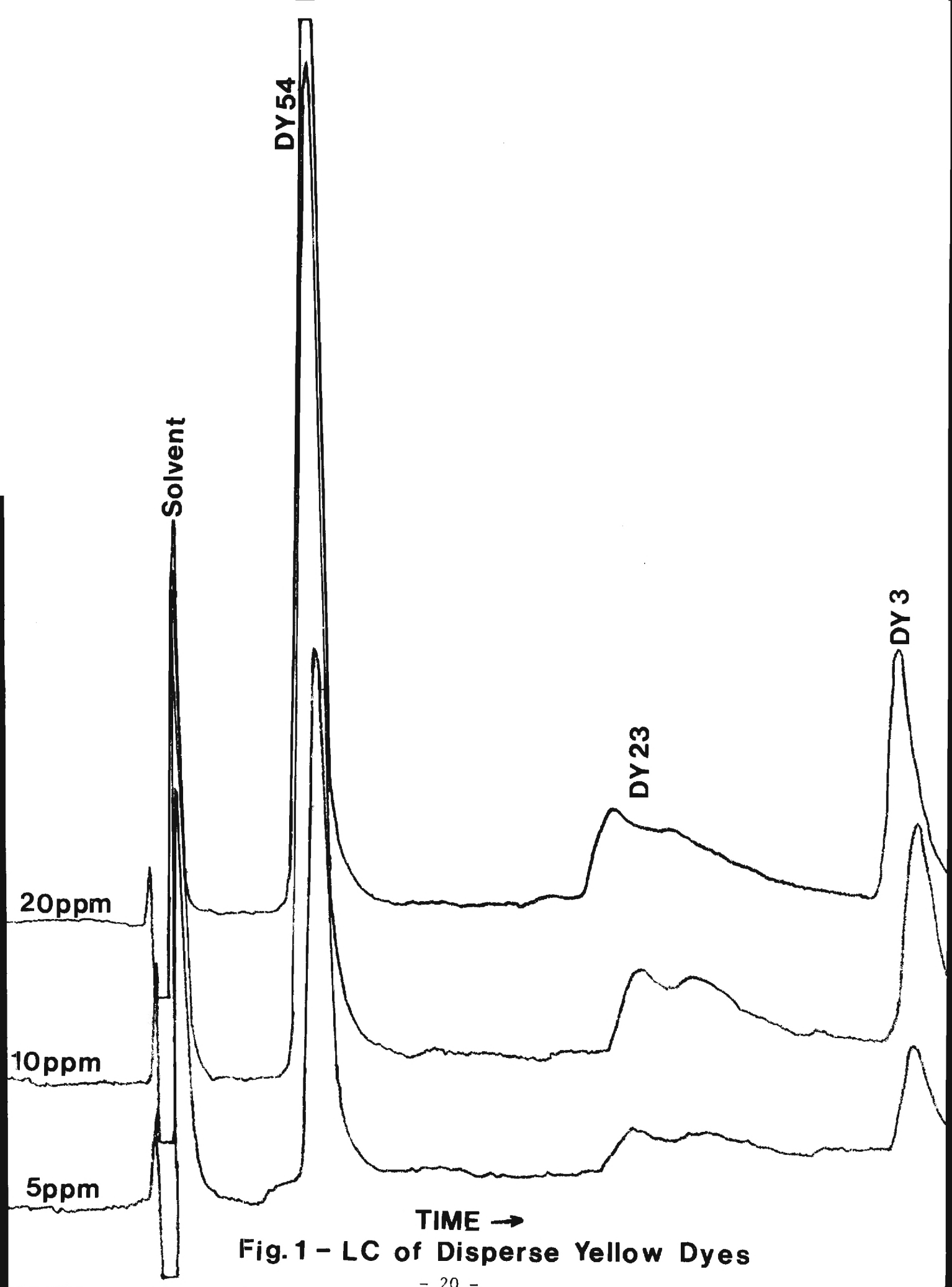

Fig. 1 – LC of Disperse Yellow Dyes

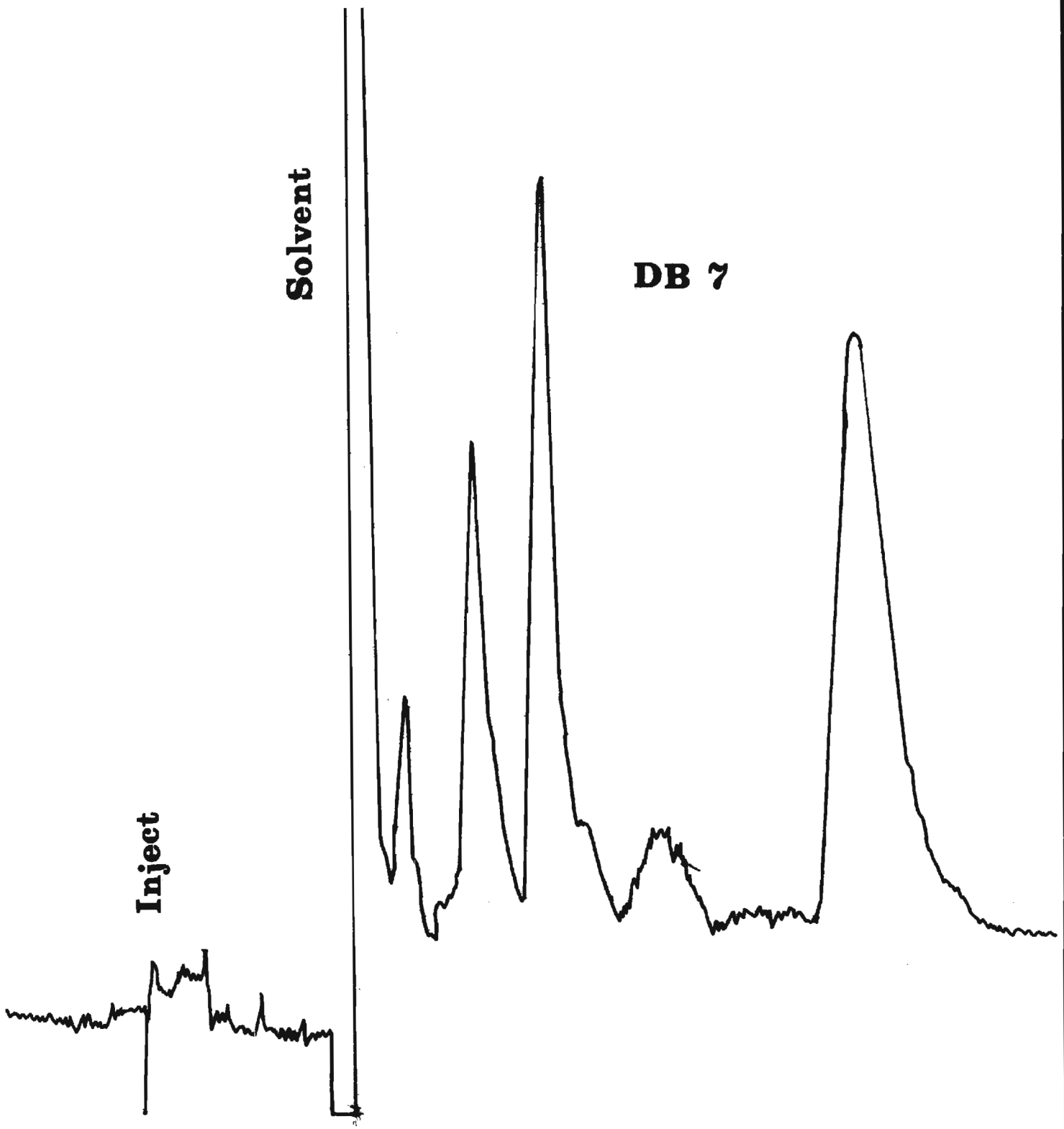

FIG. 2. LIQUID CHROMATOGRAM OF DISPERSE BLUE

to elute the red and blue dyes.

The specific systems used for the disperse dyes are detailed below.

b. Disperse Yellow Dyes

The column is first conditioned by pumping a 25/75 mixture of tetrahydrofuran/cyclohexane through the column for at least 15 minutes. A 20 µl sample of the dye mixture is injected in the solvent stream and the effluent of the column monitored at 420 nm. The composition of the solvent varied linearly from 25/75 to 100/0 tetrahydrofuran/cyclohexane over a 15 minute period. The solvent flow rate was 1 ml/minute. The resulting chromatograms of a standard 5, 10 and 20 ppm mixture of Disperse Yellow 3, 23 , and 54 are shown in Figure 1. The disperse yellows are well separated and excellent linear curves are obtained when the areas under the peaks are plotted versus concentration.

It is interesting to note that Disperse Yellow 23 gives several peaks. This dye is undoubtedly a mixture of several compounds which are partially separated by the chromatograph.

c. Disperse Red Dyes

Two separate runs on the chromatograph were required to analyze for the disperse red dyes at very low concentrations. The probable reason for this was that the red dyes are a mixture of compounds and when long elution times were used the peaks split into many components which reduce the sensitivity.

The following procedure was used with the red dyes. The column was equilibrated for 15 minutes with an 80/20 tetrahydrofuran/cyclohexane solution. Twenty µl of dye were injected and the effluent monitored at 520 nm. A flow rate of 1 ml/minute was used. Under these conditions Disperse Red 55 elutes with the solvent front and Disperse Red 60 approximately 1 to 2 minutes after the solvent front. The column is then equilibrated with a 35/65 mixture of tetrahydrofuran/cyclohexane and 20 µl of the dye mixture again injected. Under these conditions Disperse Red 55 elutes just after the solvent front and Disperse Red 60 is retained on the column. Typical chromatograms for 5, 10 and 20 ppm Disperse Red 55 are shown in Figure 3. Very similar results were obtained for Disperse Red 60. It should be noted that the detector was not set at its highest sensitivity in recording Figure 3. At highest sensitivity 1 ppm of the disperse red dyes can be very readily detected and analyzed.

d. Disperse Blue Dyes

A system similar to the one used for the disperse red dyes was used in analysis of disperse blue dyes. The column is equilibrated with 100% tetrahydrofuran at a flow rate of 1 ml/min. A 20 µl sample of the dye mixture is injected and the effluent monitored at 620 nm. The chromatogram shows a number of peaks indicating that the dye contains several components but two very distinct peaks are observed at about 2 and 4 minutes retention time. Under these conditions Disperse Blue 120 elutes with the solvent front.

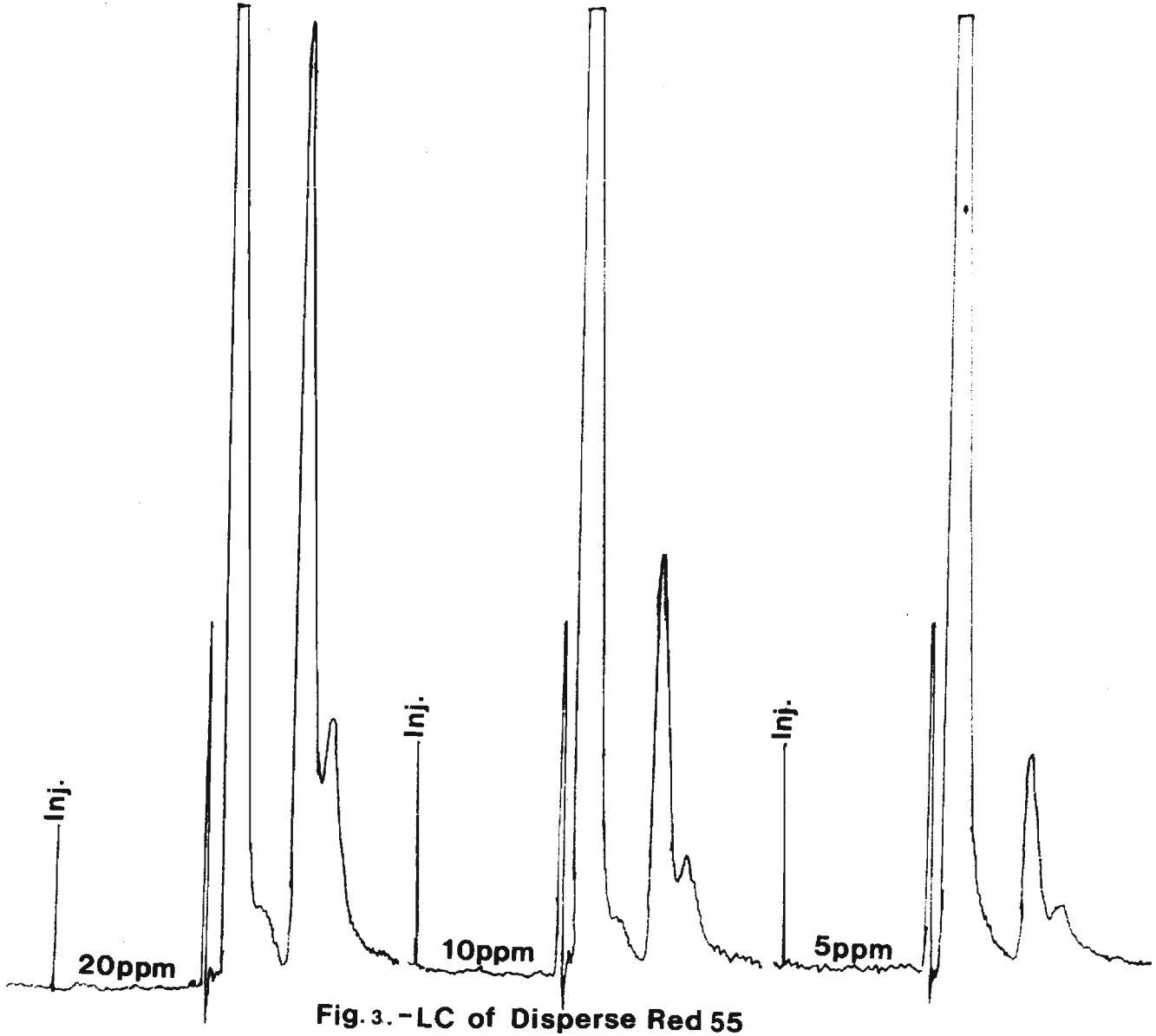

Fig. 3. - LC of Disperse Red 55

Disperse Blue 120 is determined by equilibrating the column with a 45/55 tetrahydrofuran/cyclohexane mixture and eluting with this mixture. Several peaks are observed with the principal peak at about 2 minutes retention time. Under these conditions Disperse Blue 7 is retained by the column thus providing a separation of the two blue dyes. After elution of the Disperse Blue 120 the Disperse Blue 7 is stripped by pumping 100% THF through the column.

3. Analysis for Acid Dyes

Acid dyes usually contain one or more ionizable sulfonate groups as part of the dye structure (see Appendix A). This class of dyes could probably be separated by ion exhcange liquid chromatography. However, separations are usually difficult and reproducibility is poor with ion exchange techniques.

After survey of the possible separation procedures, a technique known as paired-ion chromatography (PIC) was selected for investigation [22]. In this technique the dyes are adsorped from solution on a silica column containing C_{18} hydrocarbon groups bonded to the silica particles. The dyes are eluted with methanol-water mixtures containing tetrabutylammonium phosphate. This technique has been used to separate food dyes very similar in structure to the dyes of interest in this work [23].

The column used in the acid dye studies was a 25 cm. Spherisorb ODS (5 micron silica particles with a C-18 hydrocarbon bonded to the surface) obtained from Laboratory Data Control. The elution solvents were prepared by dissolving buffered tetrabutylammonium phosphate in methanol

and in water (the buffered tetrabutylammonium phosphate is sold under the name PIC Reagent A by Waters Associates).

Preliminary experiments using the PIC technique were conducted on known mixtures of acid yellow dyes. After several trials it was found that an elution gradient beginning at a 60 to 40 ratio of methanol to water and increasing linearly to 85/15 methanol/water over a 10 minute period gave good separation of the yellow dyes. A flow rate of 1 ml per minute was used and the detector was set at 420 nm. This same gradient was found to separate the acid red dyes and the acid blue dyes. The only change necessary for the red and blue dyes was setting the wavelength of the detector at 520 and 615 nm, respectively. Typical chromatograms for the acid yellow, red and blue dyes are shown in Figures 4, 5, and 6.

4. Quantitation of Acid Dyes

The concentrations of each of the 15 dyes was determined from the areas under the liquid chromatography peaks. The system was calibrated by running standard 5, 10 and 20 ppm solutions of each dye and determining the areas of the peaks. The areas under the peaks were obtained from the recorder integrator. Since the baseline was not always level, the areas determined from the integrator had to be corrected for the background. This was done by running the solvent or solvent program with only a "blank" (i.e., 1% DMF in benzene or methanol, the solvents used for the dyes) injected under identical instrumental conditions as the dyes and subtracting the background correction from the measured dye peak areas. Typical calibration curves are shown in Figures 7 and 8.

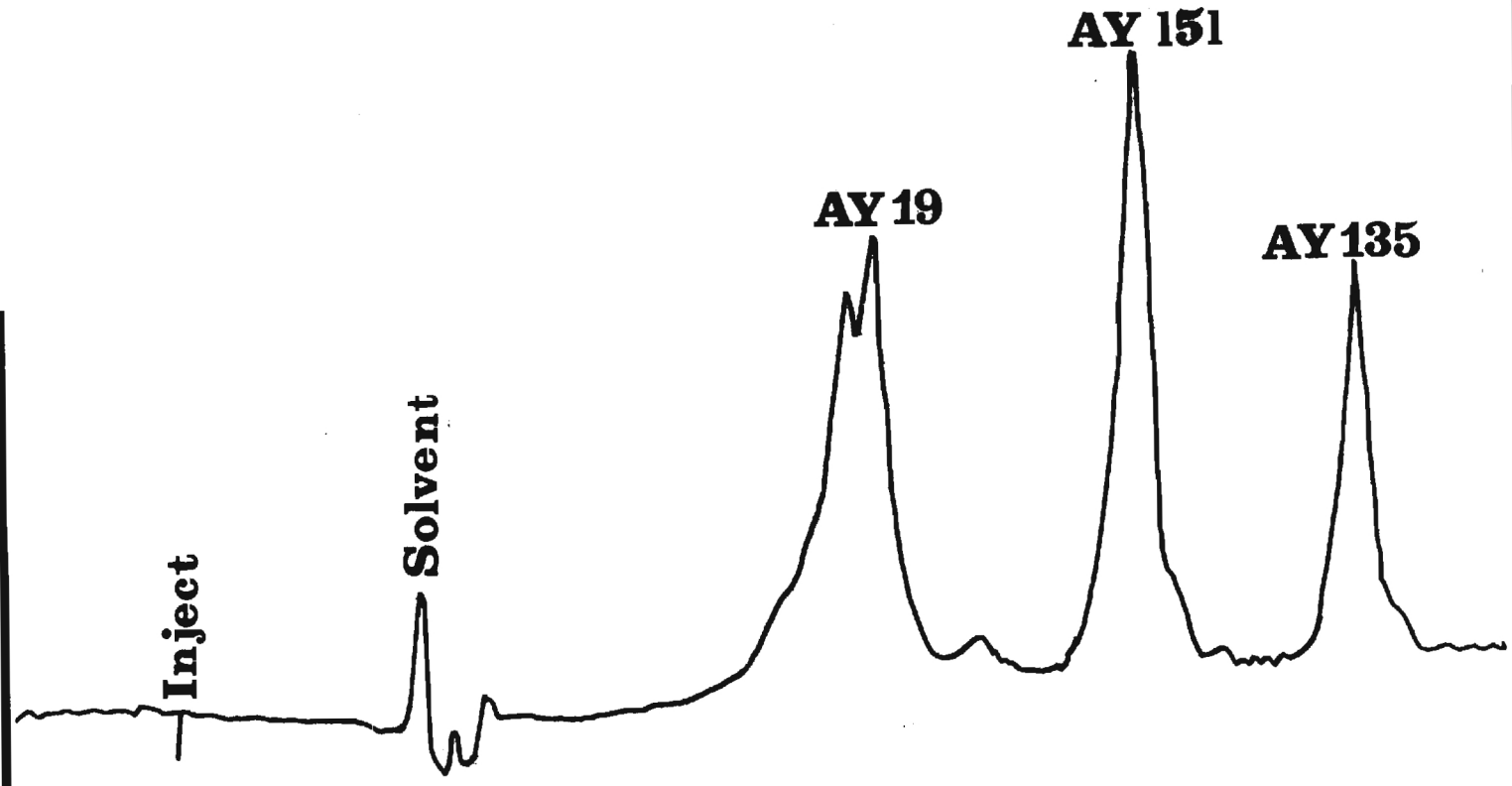

FIG. 4. LIQUID CHROMATOGRAMS OF ACID YELLOW DYES

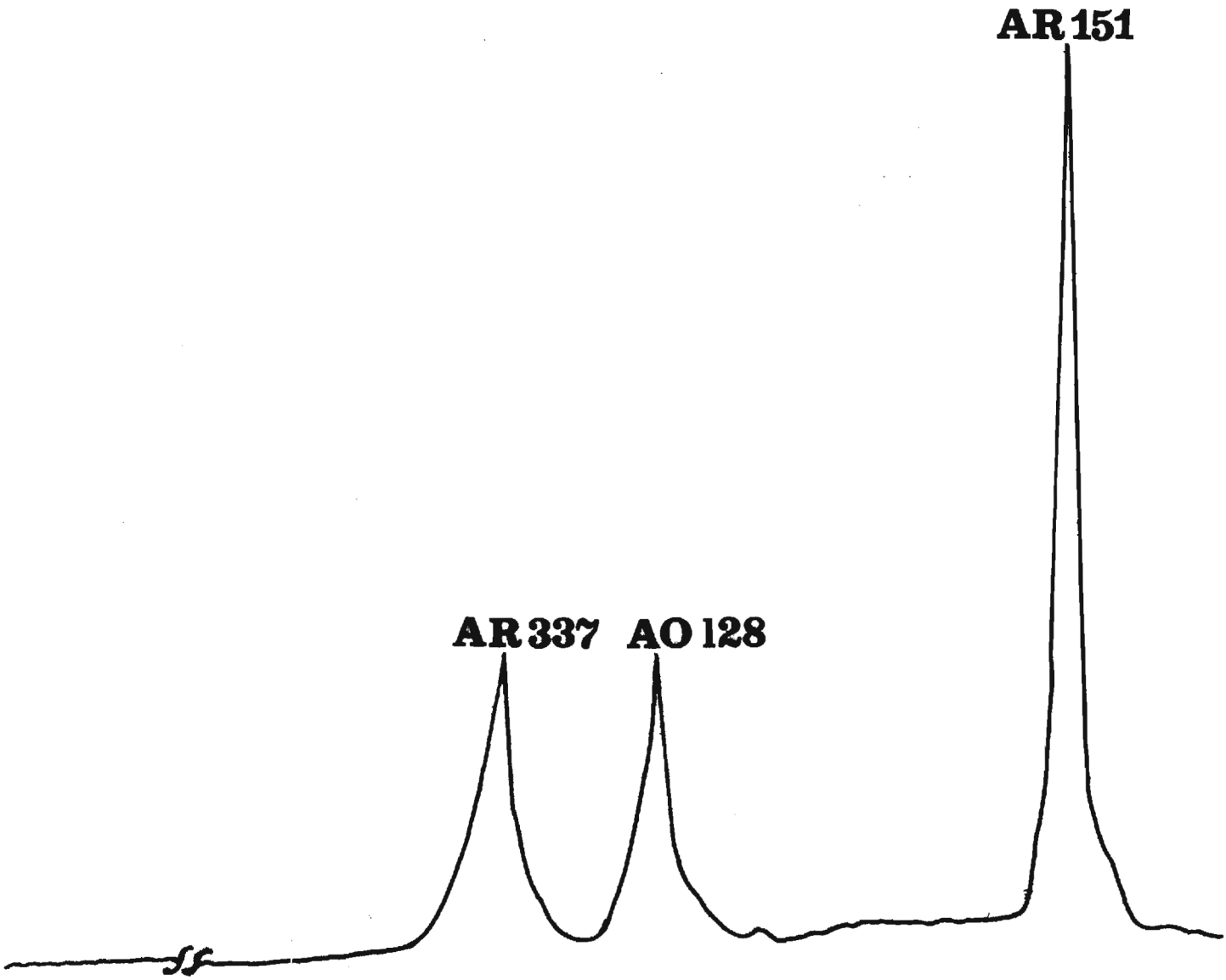

FIG. 5. LIQUID CHROMATOGRAMS OF ACID RED AND ORANGE DYES

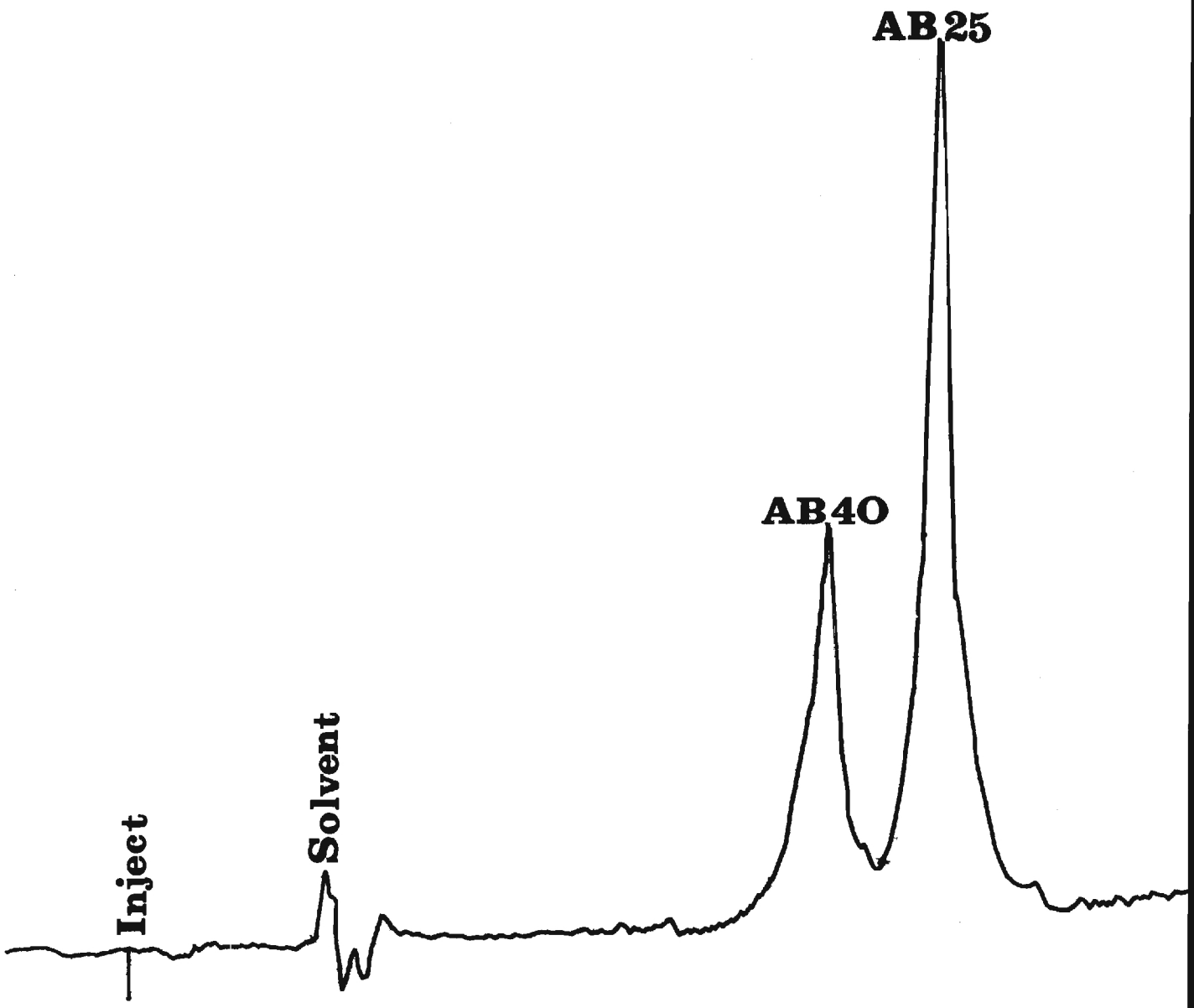

FIG. 6. LIQUID CHROMATOGRAM OF ACID BLUE DYES

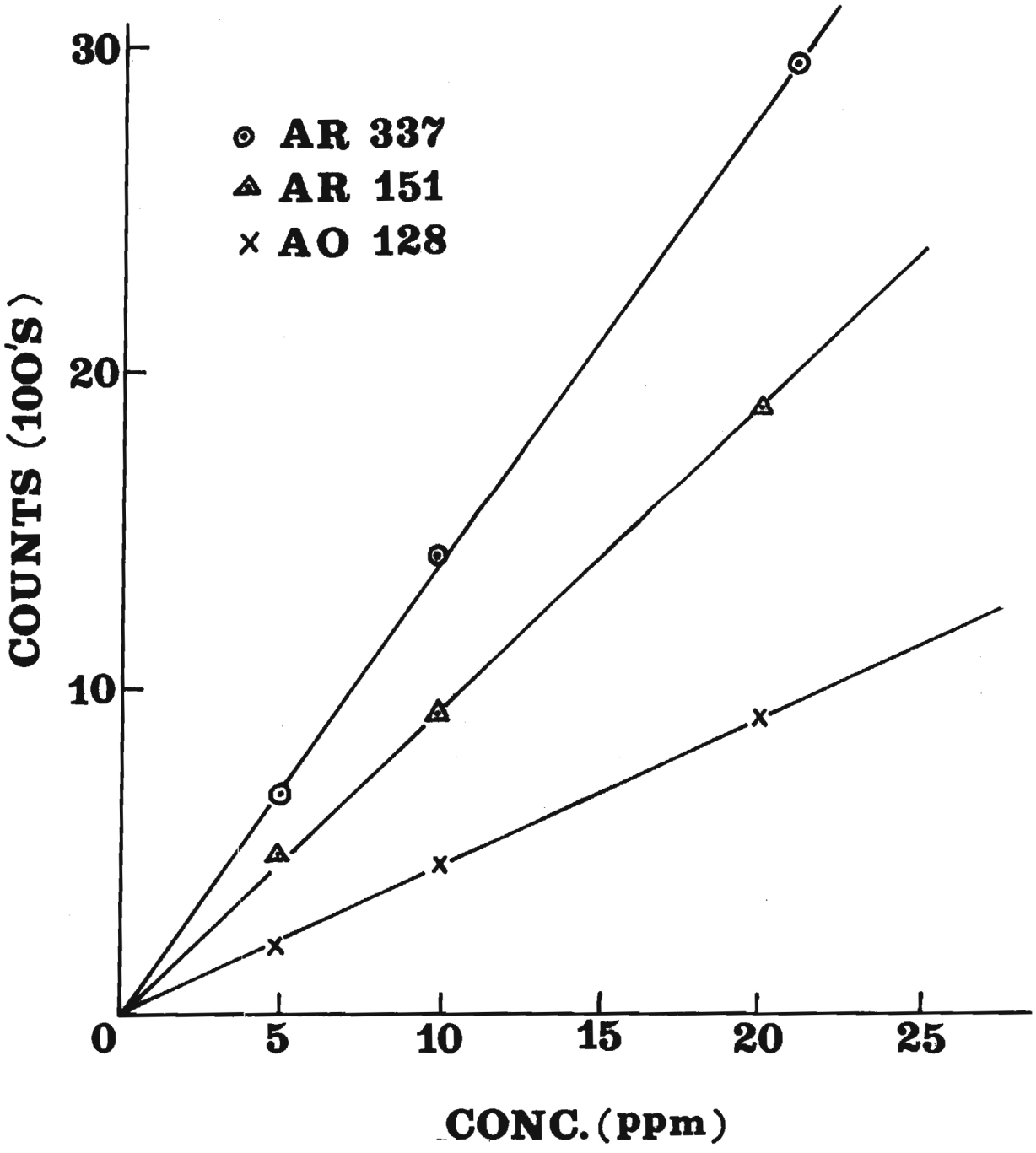

FIG. 7. ANALYTICAL WORKING CURVES FOR ACID RED AND ACID ORANGE DYES.

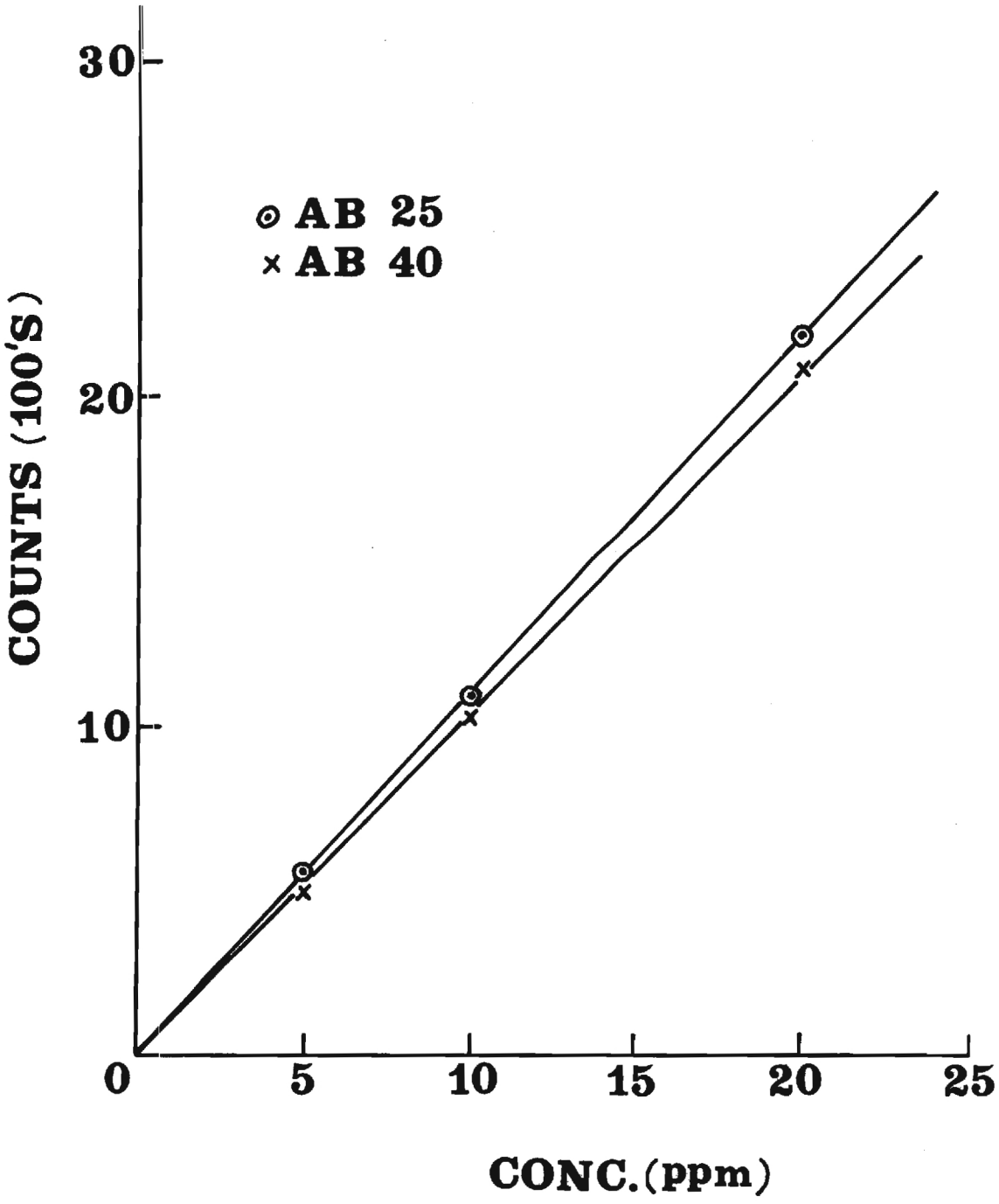

FIGURE 8. ANALYTICAL WORKING CURVES FOR ACID BLUE DYES

One other correction was required for Acid Yellow 151. Acid Orange 128 is the only color in the selected list of dyes that is not a primary color. As a result Acid Orange 128 has strong absorption in both the red and yellow regions of the visible spectrum. This situation creates no problem in analysis of the red dyes since Acid Orange 128 is well separated from Acid Red 337 and Acid Red 151 (see Figure 5). However, in the analysis of the yellow dyes, Acid Orange 128 is not separated from Acid Yellow 151. Two approaches were considered for solution of this problem. First, the selected solvent program for the yellow dyes could have been changed. This approach was not selected as it would make an otherwise very simple analytical scheme for acid dyes more complex. The second approach and the one selected was to correct the AY 151 absorption for the Acid Orange 128. In this scheme the concentration of Acid Orange 128 is determined from the adsorption at 520 nm. From the concentration and the known absorptivity at 420 nm the contribution of Acid Orange 128 at 420 nm can be subtracted to obtain the true absorption due to Acid Yellow 151.

All the other acid dyes have been examined spectrophotometrically to determine if any other similar interferences are present. Acid Orange 128 was the only problem found.

F. Discussion of the Analytical System

1. Sensitivity of the Analytical System

No tests of the absolute sensitivity of the analytical system for disperse and acid dyes have been carried out. However, use of the system for analysis of large numbers of wastewater and laboratory samples suggest that with the exception of Disperse Blue 120 and

Disperse Blue 7 the dyes can be detected by the liquid chromatograph (at highest sensitivity) at approximately 0.1 ppm. With the concentration of dyes in 1800 ml of wastewater in a volume of 10 ml by the resin adsorption procedure (giving a 180-fold increase), the system can detect 13 of the dyes at less than 1 part-per-billion (ppb) in wastewater. Under similar conditions it is estimated that Disperse Blue 7 can be detected at 10 ppb and Disperse Blue 120 at 25 ppb.

2. Performance of the Analytical System

The procedures for determining the concentration of disperse dyes in complex mixtures have been employed on several typical carpet waste samples containing known quantities of disperse dyes. This typical waste sample was prepared by dissolving appropriate quantities of the chemicals given in Table 20 of the report "Chemical Use and Discharge in Carpet Piece Dyeing" [5] in water. The sample contained not only dyes but the auxiliaries, finish components, pH control agents and other organic and inorganic compounds commonly present in dye wastewater. The quantities of each of 6 disperse dyes present in the sample are given in Table 5.

One liter of the synthetic waste sample was concentrated using the column procedure described previously. The concentrate was injected in the liquid chromatograph and the quantities of each of the six dyes found in the known waste sample are given in Table 5 as well as the percent of the known that was found. Results indicate that greater than 70% of most disperse dyes are detected. The results

Table 5

Analysis of Known Mixture

Dye	Conc. in Waste Known (mg/L)	Conc. in Waste Found (mg/L)	% Found
DY 54	5.67	4.05	70
DY 3	5.78	5.31	92
DY 23	8.21	5.44	66
DR 60	3.97	3.44	87
DR 55	1.82	1.27	70
DB 7	1.82	1.18	65

agree closely with the previous studies on dye recovery (Table 3) by the resin adsorption system and suggest that improvements in this system should be investigated.

Part II

Analysis of Coosa River Basin Samples For Acid and Disperse Dyes

A. Samples

The analytical techniques described in the previous section have been used to analyze a number of samples from the Coosa River basin. The Coosa River and its tributaries carry over 50% of all carpet dyeing wastewater in the United States. A map of the Coosa basin in Georgia is shown in Figure 9. The cities of Dalton, Chatsworth, Calhoun, Cartersville and Rome are all major centers for carpet production. The city of Dalton is the principal center with the Dalton River Bend Waste Treatment plant receiving approximately 25% of all U.S. carpet dyeing wastewater.

Grab samples were collected in the Coosa basin at three different times during 1976-1977. The first set of samples was collected on October 28, 1976, the second set on March 8 and 9, 1977, and the third set on June 7 and 8, 1977. The samples collected March 8 and 9 were collected at times selected to correspond with times at which dyes should have been at peak concentration at the collection site.

The peak period in dyeing of carpet in the Dalton area occurs during the day shift on Mondays through Thursdays. This results in a peak flow at the Dalton waste treatment plant usually between 3 and 5 in the afternoon of those days. Friday is generally a "clean-up" day and most plants are closed on weekends except during peak periods of production. An attempt was made to collect samples in the Coosa basin at times such that the samples would reflect the peak flows at the Dalton waste treatment plant and contain maximum dye concentrations.

Mr. Gary Ellis of the Environmental Protection Division provided flow times in the Coosa basin based on a computer simulation of stream flow. Volumes and flow times based on this model for the week of March 7 are shown in Table 6.

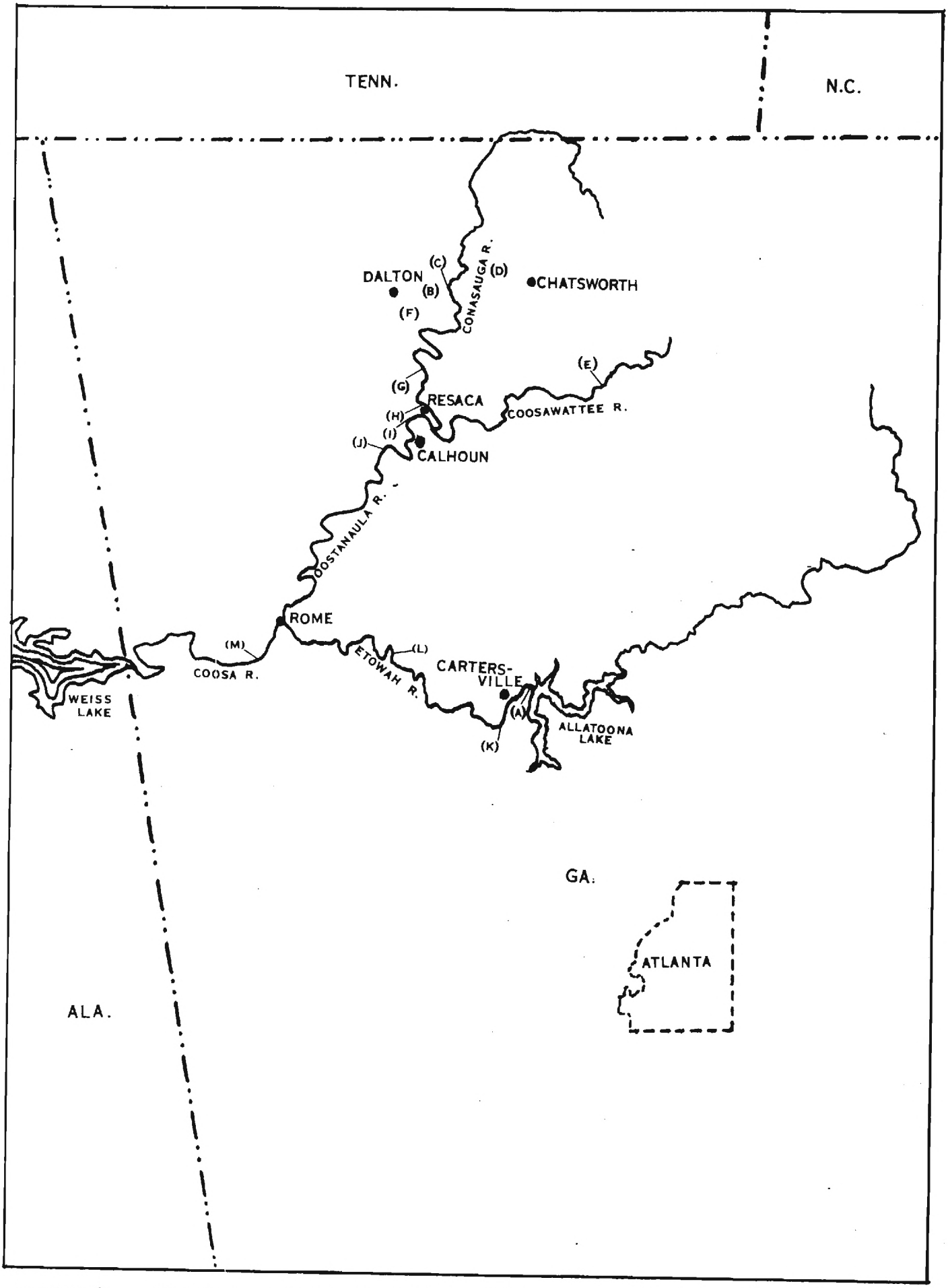

FIGURE 9. -- The Coosa River Basin with location of centers of carpet manufacturing

Table 6

Flow Times in Coosa Basin - March 7, 1978

Site	Flow	Time
Dalton Water Intake	—	0
Tibbs Bridge	52 cfs	13-15½ hours
Dalton Waste Treatment Outfall	—	12-14½ hours
Looper's Bridge	789 cfs	1 hour (from DWTP)
Tilton Bridge	884 cfs	15-18½ hours (from DWTP)
Calhoun Water Intake	2550 cfs	22-26½ hours (from DWTP)
Rome Water Intake	2640 cfs	30-35 hours (from DWTP)

During the week selected for sampling the carpet industry in Dalton was operating at 80 - 90% of normal production capacity based on total flow at the Dalton waste treatment plant. Residence time in the Dalton waste treatment plant is approximately 24 hours. The effluent on any given day is therefore representative of the influent received the previous day.

The day and hour of collection at the various sites is shown in Table 7. The table also gives the estimated time that the sample was leaving the Dalton waste treatment plant. The sample collected at the Georgia Highway 40 bridge over the Oostanula River was collected at a time such that the sample was entering the Calhoun Waste Treatment plant Tuesday, March 8 at approximately 2:00 P.M.

All samples were refrigerated at the collection site and were kept at 0°C until the concentration step.

A third sampling trip was conducted on June 7 and 8. This time was selected to take advantage of the low flows experienced in early June. Samples were collected in the Rome area on June 7 and in the Dalton and Calhoun area on June 8. These samples were numbered 129-30-1 to 129-32-5. All samples were refigerated immediately after collection and remained refrigerated until concentrated except finish water samples. Finish water samples were refrigerated within 8 hours of collection. Three mud samples were collected to determine the quantity of dyestuffs that may be adsorbed on mud in the Coosa basin. These samples required a different extraction procedure as outlined below.

A complete list of all samples collected is given in Table 8. As reflected in the sample collection special emphasis was placed on analysis

Table 7

Sample Collection Times

	Site	Time Collected	Time Left Dalton Waste Treatment Plant
129-22-1	Dalton Waste Treatment Plant Influent	Wed., Mar. 9, 4:00 PM	Thur., Mar. 10, 4:00PM
129-22-2	Dalton Waste Treatment Plant Effluent	Wed., Mar. 9, 4:20 PM	Wed., Mar. 9, 4:20PM
129-22-3	Looper's Bridge	Wed., Mar. 9, 5:00 PM	Wed., Mar. 9, 4:00PM
129-22-4	Tilton Bridge	Thurs., Mar. 10, 9:00 AM	Wed., Mar. 9, 4:00PM
129-23-5	Calhoun Raw Water	Thurs., Mar. 10, 10:00 AM	Tues., Mar. 8, 4:00PM
129-23-6	Calhoun Finish Water	Thurs., Mar. 10, 10:30 AM	Tues., Mar. 8, 4:00PM
129-23-7	Calhoun Filter Backwash Plant Influent	Thurs., Mar. 10, 11:00 AM	Tues., Mar. 8, 4:00PM
129-23-8	Calhoun Waste Treatment Plant Influent	Thurs., Mar. 10, 12:30 PM	— —
129-23-9	Calhoun Waste Treatment Plant Effluent	Thurs., Mar. 10, 12:50 PM	— —
129-23-10	Georgia Highway 40 Bridge (Oostanaula)	Thurs., Mar. 10, 2:00 PM	— —

Table 8

Coosa Basin Samples Collected

Sample	Collection Site	Time of Collection	
129-10-2	Dalton Raw Water Intake	10/28/76	11:45 A.M.
129-11-5	Dalton Waste Treatment Plant Influent	10/28/76	3:15 P.M.
129-11-8	Dalton Waste Treatment Plant Effluent	10/28/76	4:15 P.M.
129-12-9	Looper's Bridge	10/28/76	5:15 P.M.
129-22-1	Dalton Waste Treatment Plant Influent	3/9/77	4:00 P.M.
129-22-2	Dalton Waste Treatment Plant Effluent	3/9/77	4:20 P.M.
129-22-3	Looper's Bridge	3/9/77	4:45 P.M.
129-23-4	Tilton Bridge	3/10/77	9:00 A.M.
129-23-5	Calhoun Raw Water Intake	3/10/77	10:00 A.M.
129-23-6	Calhoun Finish Water	3/10/77	10:30 A.M.
129-23-7	Calhoun Filter Backwash	3/10/77	11:00 A.M.
129-23-8	Calhoun Waste Treatment Plant Influent	3/10/77	12:30 P.M.
129-23-9	Calhoun Waste Treatment Plant Effluent	3/10/77	12:50 P.M.
129-23-10	Oostananla Bridge at Ga. Highway 140	3/10/77	1:45 P.M
129-30-1	Rome Raw Water Intake	6/7/77	9:20 A.M.
129-30-2	Rome Finish Water	6/7/77	9:35 A.M.
129-30-3	Rome Waste Treatment Plant Influent	6/7/77	3:35 P.M.
129-30-4	Rome Waste Treatment Plant Effluent	6/7/77	4:00 P.M.
129-30-5	Looper's Bridge	6/7/77	5:45 P.M.

Table 8 (cont'd.)

Sample	Collection Site	Time of Collection	
129-31-1	Looper's Bridge Mud Sample	6/8/77	6:00 PM
129-31-2	Tilton Bridge	6/8/77	10:30 A.M.
129-31-3	Tilton Bridge Mud Sample	6/8/77	10:55 A.M.
129-32-1	Calhoun Water Intake	6/8/77	11:30 A.M.
129-32-2	Calhoun Water Intake Mud Sample	6/8/77	11:30 A.M.
129-32-3	Calhoun Finish Water	6/8/77	11:45 A.M.
129-32-4	Calhoun Waste Treatment Plant Influent	6/8/77	1:15 P.M.
129-32-5	Calhoun Waste Treatment Plant Effluent	6/8/77	1:30 P.M.

of city water supplies in the Coosa basin.

B. Analysis of Collected Water and Wastewater Samples

The collected stream, finish water, and filter backwash water samples were concentrated using the XAD-2 resin system. These samples were concentrated 180-fold (1800 ml ⟶ 10 ml). The influent and effluent waste treatment plant samples were generally concentrated only 36-fold (1800 ml → 50 ml) due to the higher dye concentrations in these samples.

Twenty microliter samples of the extracts were injected into the liquid chromatograph and analyzed by the procedure previously described. Results of the analysis for disperse dyes are given in Table 9 and for acid dyes in Table 10. It should be noted that, due to a loss of part of the concentrate, data on disperse dyes were not obtained for samples 129-11-8 and 129-12-9.

C. Analysis of Mud Samples

During the June 7 and 8 sampling trip, mud samples were collected at the Looper's Bend Bridge, at the Tilton Bridge and near the intake of the Calhoun water treatment plant. The dry mud samples were concentrated by placing 100 gram samples in a Soxhlet extractor and extracting with benzene followed by methanol and then by the pyridine, ammonium hydroxide and tetrahydrofuran mixture for 24 hours. The same extracting solvent was used for subsequent 100 gram samples until a total of 1000 grams of mud had been extracted. The extracts were rotavapped to dryness and taken up in either 50 or 25 ml of solvents for liquid chromatographic analysis. The concentration factor for samples 129-31-3 and 129-32-1 was 40 and for sample 129-31-1 the factor was 20.

Table 9

Concentration of Disperse Dyes (parts-per-billion) in Samples Taken from the Coosa River Basin

Sample	DY 3	DY 23	DY 54	DR 55	DR 60	DB 7	DB 120
129-10-2	-	-	-	-	-	-	-
129-11-5	32	458	27	187	78	97	198
129-22-1	77	36	7	67	16	62	<25
129-22-2	+	17	9	24	14	35	<25
129-22-3	<1	3	+	-	+	-	-
129-23-4	<1	3	+	+	-	-	-
129-23-5	-	-	-	-	-	-	-
129-23-6	<1	-	-	-	-	-	-
129-23-7	<1	-	-	-	+	-	-
129-23-8	436	257	6	38	6	85	38
129-23-9	17	10	2	26	6	152	37
129-23-10	1	-	-	-	+	-	-
129-30-1	1	+	-	-	-	-	-
129-30-2	-	-	-	-	-	-	-
129-30-3	222	93	13	4	52	19	57
129-30-4	256	120	32	11	76	26	114
129-30-5	3	2	5	3	-	22	<25
129-31-2	<1	-	-	-	-	-	-
129-32-2	-	-	-	-	-	-	-
129-32-3	-	-	-	-	-	-	-
129-32-4	209	77	3	86	21	239	56
129-32-5	+	36	<1	20	-	139	56

\- dye not detected

\+ dye detected but below minimum concentration for quantitation

Table 10

Acid Dye Concentration (in ppb) in
Coosa Basin Samples

Sample	AY-19	AY-151	AY-135	AB-40	AB-25	AR-337	AO-128	AR-151
129-10-2	+	-	-	-	-	-	-	-
129-11-5	1440	+	-	58	53	101	41	7
129-11-8	378	+	-	-	11	190	17	8
129-12-9	156	+	-	-	-	26	-	2
129-22-1	1200	1110.	-	114	145	-	-	62
129-22-2	617	104	-	352	245	1020	+	77
129-22-3	+	8	-	21	16	42	-	8
129-23-4	62	-	-	29	15	42	-	3
129-23-5	38	-	-	-	-	8	-	1
129-23-6	-	-	-	-	-	-	-	-
129-23-7	-	-	-	-	-	-	-	-
129-23-8	127	57	+	253	54	56	137	7
129-23-9	212	132	+	403	74	28	269	76
129-23-10	-	-	-	-	-	+	-	+
129-30-1	10	-	-	-	-	-	-	-
129-30-2	-	-	-	-	-	-	-	-
129-30-3	23	134	-	+	18	69	49	5
129-30-4	301	3750	-	22	502	78	1120	48
129-30-5	9	+	-	7	42	89	15	1
129-31-2	172	+	-	+	14	19	-	-
129-32-2	32	-	+	-	-	5	-	-
129-32-3	-	4	-	-	+	-	-	-
129-32-4	99	119	130	87	32	13	-	-
129-32-5	172	-	-	197	27	-	+	-

- dye not detected

+ dye detected but below minimum concentration for quantitation

Results of the analysis of the mud samples for disperse dyes is given in Table 11. Results of the analysis for acid dyes is given in Table 12.

D. Discussion of Results

The immediate conclusion which the results suggest is that acid dyes are present in higher concentration than disperse dyes in the Coosa River basin. There are probably 2 factors accounting for this difference. First, the carpet industry is tending more toward use of acid dyes for dyeing nylon carpet. This is due in part to the increasing use of continuous dye ranges which require acid dyes. Also, acid dyes are being used with increasing frequency in beck dyeing to meet more stringent light and ozone stability requirements. Second, later studies (see Part III) suggest that disperse dyes are more readily removed by biological waste treatment systems than acid dyes. Similarly, since disperse dyes are not in solution but are dispersed as small particles in water, they are probably more readily removed by stream sediments than acid dyes. This is suggested by comparison of the results of the analysis for acid and disperse dyes on the mud samples (Tables 11 and 12).

The influents and effluents of the Dalton, Calhoun and Rome waste treatment plants show appreciable concentrations of all 15 dyes with the exception of Acid Yellow 135. This dye is quite easily detected in the analytical system so its absence suggests that it is not being used as extensively in carpet dyeing as was the case previously. It is interesting to note that

Table 11

Analyses of Mud Samples for Disperse Dyes
(parts-per-billion based on dry mno weight)

Sample No.	Site	DY 3	DY 23	DY 54	DR 55	DR 60	DB 7	DB 120
129-31-1	Looper's Bridge	420	2970	1600	-	3400	1405	3000
129-31-3	Tilton Bridge	455	1350	970	+	1050	625	3250
129-32-1	Calhoun Water Intake	140	114	31	119	19	-	62

- dye not detected

+ dye detected but below minimum concentration for quantitation

Table 12

Analysis of Mud Samples for Acid Dyes
(parts-per-billion)

Sample No.	Site	AY-19	AY-151	AY-135	AB-40	AB-25	AR-337	AD-128	AR-151
129-31-1	Looper's Bridge	2080	515	+	225	550	205	790	27
129-31-3	Tilton Bridge	1168	1105	+	113	315	173	615	35
129-32-1	Calhoun Water Intake	110	165	-	-	+	-	-	15

- dye not detected

+ dye detected not below minimum concentration for quantitation

disperse dyes are in relatively higher concentration at Rome and Calhoun and acid dyes in higher concentrations at Dalton. This probably reflects differences in dyeing processes (i.e., more continuous dyeing at Dalton) in the three cities.

In several cases the waste treatment plant effluents show higher dye concentrations than the influents. Since all samples were "grab" samples this is undoubtly due to daily and time of day variation in concentration of the various dyes. Wide fluctuation in acid dye concentrations can result from discharge of unused dye paste at the end of continuous runs.

Downstream below the outfall of the Dalton waste treatment plant, river samples collected at Looper's Bridge and Tilton Bridge show low concentrations of a few acid and disperse dyes. No disperse dyes were present in the raw water intake at the Calhoun water treatment plant. Small quantities of Acid Yellow 19 and traces of Acid Red 337 and Acid Red 151 were present in the Calhoun raw water. Calhoun finish water was free of dye except for one sample which contained 4 ppb of Acid Red 151. The Rome raw water contained 10 ppb of Acid Yellow 19 and a trace of Disperse Yellow 3 but no dyes were detected in the Rome finish water.

Mud samples collected at Looper's Bridge, Tilton Bridge and at the Calhoun raw water intake all show appreciable quantities of both acid and disperse dyes.

The results suggest that the developed analytical system can be readily applied to dye analysis for both waste treatment plant and stream samples. Analysis of composite samples will probably be necessary to obtain the best data on dye concentrations.

Part III

Removal of Dyes from Carpet Dyeing Wastewater by Biological and Advanced Treatment Systems

A. Samples

The system of analyses for acid and disperse dyes has been applied to several carpet dyeing wastewater samples that have been subjected to various waste treatment procedures.

Initial studies were carried out on synthetic carpet waste samples treated in a bench scale model of an activated sludge system [24]. The synthetic waste sample was prepared by mixing appropriate quantities of the dyes and chemicals listed in Table 20 of Reference 5. The synthetic carpet dyeing wastewater was fed continuously to a Horizon Bio-Oxidation System [25]. The system was seeded with a sample of acclimated sludge from the Dalton waste treatment plant. After allowing the bio-oxidation system to achieve equilibrium, samples of effluent were collected over a 10 day period and analyzed for 6 disperse dyes. The influent and 10 samples of the effluent were analyzed. The results are shown in Table 13 (the data for Disperse Blue 7 are for the major component which elutes first in the liquid chromatogram). The results suggest that biological oxidation can remove better than 60% of most disperse dyes from dyeing wastewater. The mechanism of removal is probably adsorption on the sludge rather than true biological oxidation.

Dye analysis was also used to evaluate, in part, the effectiveness of various advanced treatment systems in removal of disperse and acid dyes from carpet dyeing wastewater. The treatment systems were set-up at the Dalton River Bend Waste Treatment Plant as part of a research project conducted under the direction of Wiedeman and Singleton Consulting Engineers.

Table 13

Removal of Disperse Dye by Biological Oxidation
of Carpet Dye Wastewater

Sample	DY 54		DY 3		DY 23		DR 55		DR 60		DB 7	
	Mg/L	Removal	Mg/L	Removal	Mg/L	Removal	Mg/L	Removal	Mg/L	Removal	Mg/L	Removal
Influent	4.05	—	5.31	—	5.44	—	1.27	—	3.44	—	1.18	—
Effluent 1	0.98	76	0.95	82	1.13	70	0.23	82	2.46	28	0.29	75
Effluent 2	1.45	64	0.53	90	1.85	66	0.32	75	2.77	19	0.53	55
Effluent 3	0.74	82	0.37	93	2.34	57	0.29	77	1.48	57	0.60	49
Effluent 4	0.73	83	0.37	93	1.79	67	0.24	81	1.33	61	0.66	99
Effluent 5	0.68	83	0.21	96	2.28	58	0.11	91	0.88	74.	0.53	55
Effluent 6	0.96	76	0.16	97	1.90	65	0.22	83	0.48	86	0.32	73
Effluent 7	0.73	82	0.22	96	1.47	73	0.19	85	1.42	59	0.45	62
Effluent 8	1.01	75	0.32	94	1.74	68	0.29	77	1.22	65	0.41	65
Effluent 9	0.88	78	0.16	97	1.82	72	0.24	81	1.06	69	0.28	76
Effluent 10	1.03	75	0.32	94	2.12	61	0.62	51	0.84	76	0.16	86

The samples analyzed as part of this project were collected as indicated in Figure 10. The samples are identified in Table 14. The Reactor Effluent samples were collected at the clarifer effluent of the Dalton waste treatment plant (extended aeration activated sludge system). This effluent was then subjected to dual media filtration (24518 and 24705) followed by ozone treatment (24519 and 24706). The reactor effluent was also subjected to flocculation followed by sedimentation (19189 and 19237) and to dual media filtration followed by carbon adsorption (19188 and 19240). All samples were 48 hour composites collected in 1 gallon glass containers. They were refrigerated at 0°C until subjected to the resin concentration procedure.

B. Results of Analysis for Acid and Disperse Dyes

The wastewater samples from the Dalton waste treatment plant and samples of effluents from the various advanced treatment processes were concentrated by macroreticular resin adsorption and the concentrates (dye in 1800 ml wastewater concentrated in 10 ml) separated and quantitated by liquid chromatography as detailed in Part I. Results of the analysis for disperse dyes are given in Table 15. Results of acid dye analysis are shown in Table 16.

C. Discussion of Results

As indicated in Table 15, the concentration of disperse dyes in the effluent of the Dalton waste treatment plant are very low. This probably again reflects the effectiveness of an activated sludge treatment system for removal of disperse dyes. The levels of disperse dyes in these reactor

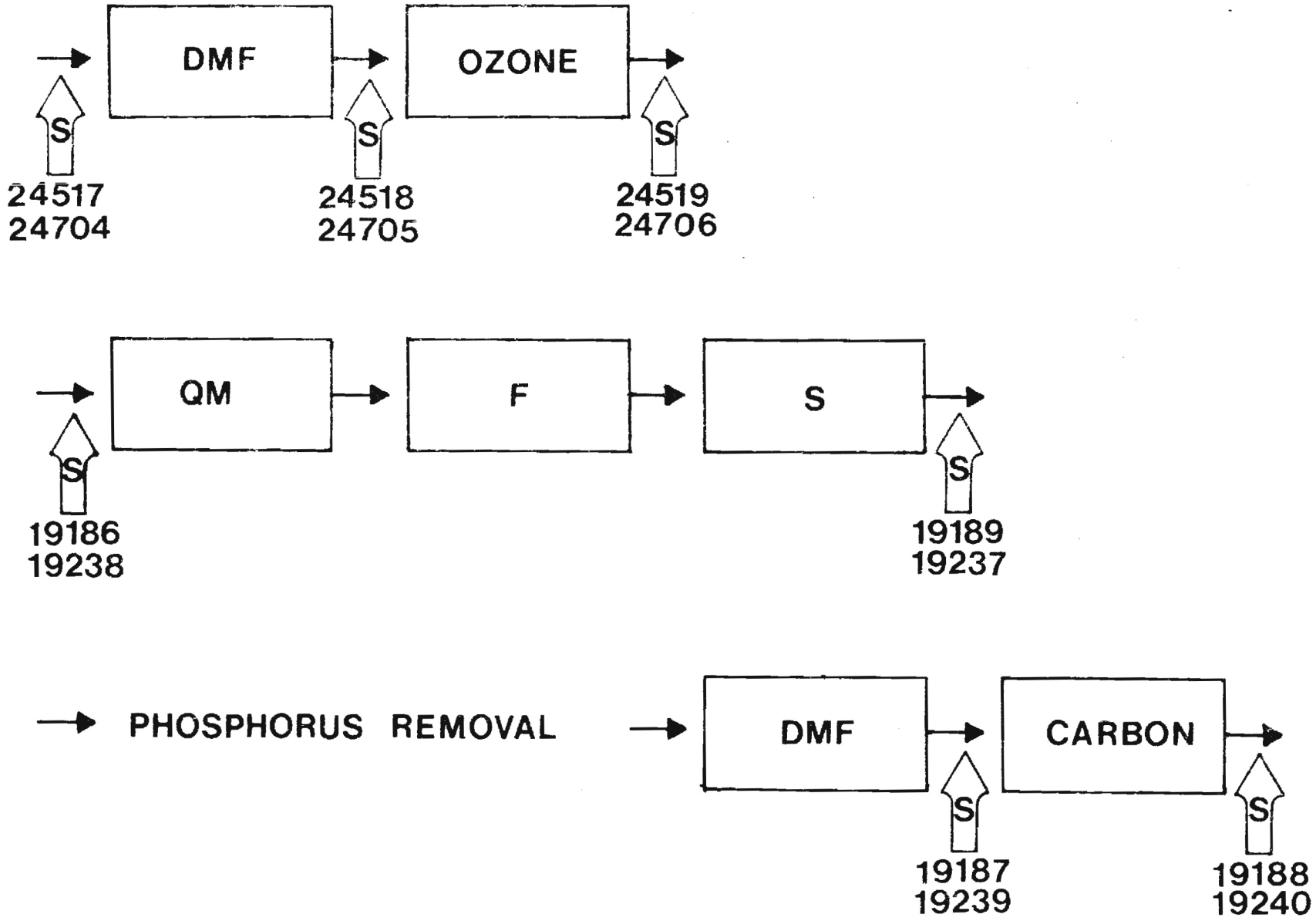

FIGURE 10. SAMPLES COLLECTED FOR EVALUATION OF ADVANCED WASTE TREATMENT SYSTEMS

Table 14

Samples for Dye Analysis

Sample	Location	Date
24517	Reactor Effluent	July 5-7
24518	Dual Media Filter Effluent	July 5-7
24519	Ozone Treatment Effluent	July 5-7
24704	Reactor Effluent	July 12-14
24705	Dual Media Filter Effluent	July 12-14
24706	Ozone Treatment Effluent	July 12-14
19186	Reactor Effluent	May 18-20
19189	Mixed Liquor Before P Removal	May 18-20
19187	Dual Media Filter Effluent	May 18-20
19188	Activated Carbon Effluent	May 18-20
19238	Reactor Effluent	May 23-25
19237	Mixed Liquor Before P Removal	May 23-25
19239	Dual Media Filter Effluent	May 23-25
19240	Activated Carbon Effluent	May 23-25

Table 15

Disperse Dyes in Samples Collected in Dalton
Waste Treatment Plant Study

(ppb)

Sample	DY 3	DY 23	DY 54	DR 55	DR 60	DB 7	DB 120
19186	+	- *	1.8	3.0	5.5	+	-
19187	+	- *	1.3	3.0	2.3	+	-
19188	+	+	+	+	+	-	-
19189	+	- *	+	+	+	-	-
19237	+	+	+	+	+	+	-
19238	+	2.2	+	-	+	+	-
19239	+	1.6	+	-	+	+	-
19240	1.9	2.8	+	-	+	-	-
24517	+	+	2.1	+	+	-	-
24518	+	+	1.1	+	+	-	-
24519	+	1.2	+	-	1.7	-	-
24704	+	+	1.4	1.6	+	+	-
24705	+	- *	1.1	2.3	+	+	-
24706	+	1.8	-	2.0	+	-	-

\+ dye detected but concentration less than 1 ppb

\- dye not detected

* dye may be present in very low concentration but interference by an impurity prevents quantitation.

Table 16

Acid Dyes in Samples Collected in Dalton
Waste Treatment Plant Study
(ppb)

Sample	AY19	AY151	AY135	A0128	AR337	AR151	AB40	AB25
24517	+	-	-	+	263	+	33	116
24518	-	190	_	+	268	+	47	107
24519	285	-	-	+	104	-	15	46
24704	-	-	-	56	541	4	174	209
24705	-	-	-	28	443	-	178	186
24706	+	-	-	-	-	-	-	-
19186	302	19	-	13	49	4	32	88
19189	-	63	8	+	21	5	8	17
19187	+	9	-	+	14	+	54	214
19188	+	-	-	-	+	-	+	7
19238	-	-	-	-	499	4	44	182
19237	+	32	-	14	19	11	18	33
19239	+	+	-	+	427	2	54	144
19240	-	-	-	-	+	2	14	11

\+ dye detected but concentration less than 1 ppb

\- dye not detected

effluent samples are lower than those observed previously for Dalton waste treatment plant effluents (see Part II). This difference is probably due to the fact that samples analyzed in Part II were grab samples taken at the time of peak carpet dyeing waste flow and should reflect maximum dye concentrations. The samples collected for this study were composites taken over a 48 hour period and more nearly reflect average concentrations.*

Although the disperse dye concentrations are all quite low, analysis of the advanced treatment system effluents suggest that with the exception of flocculation and sedimentation these treatment techniques are not particularly effective in removing disperse dyes from wastewater.

The results of the analysis for acid dyes (Table 16) confirm previous results (Part II) that acid dye concentrations are higher in the Dalton waste treatment plant effluents than disperse dye concentrations. The acid dye concentrations show wide fluctuations among the various waste treatment plant effluent samples. These fluctuations may result from discharge of concentrated dye solutions used in continuous dyeing of carpet.

Analysis of the advanced treatment systems effluents suggest that dual media filtration is virtually useless in removing acid dyes (compare Samples 24517 with 24518 and Samples 24704 with 24705). Ozone treatment is effective as can be seen from comparison of Samples 24518 and 24519 and Samples 24705 and 24706. Carbon adsorption is also very effective for removal of acid dyes (compare 19187 with 19188 and 19239 with 19240).

One of the more interesting conclusions from this work is that either ozone or carbon adsorption treatment following biological oxidation should provide a good system for removal of dyes from carpet dyeing wastewater.

* It was learned later that these samples had been chemically coagulated and clarified prior to submission for analysis [29]

Biological treatment should effectively remove disperse dyes and the ozone or carbon adsorption remove acid dyes. Carbon adsorption in conjunction with biological treatment appears to be particularly effective as indicated by the very low dye concentrations in samples 19188 and 19240.

PART IV

Improvement and Extention of the Dye Analysis System

A. Introduction

As noted in Part I, the recovery of dyes from the macroreticular resin column is one aspect of the analytical system which could be improved. Although recoveries of all dyes were greater than 70%, it was felt that this could be improved by modifications in the recovery procedure. This aspect of the dye analysis system was investigated for more efficient dye recovery.

Extension of the dye analysis system to a second major class of dyes, direct dyes, has been investigated also. Direct dyes are used extensively in dyeing of cotton textiles and are the major dyes used in coloration of paper products. The similarity of structure between acid dyes and direct dyes suggested that the analytical system might also be applicable to this important dye class.

B. Improved Dye Recovery System

Spectrophotometric analysis of the column effluents from the XAD-2 resin adsorption of dye from water-DMF solvent mixtures showed that acid and disperse dyes are quantitatively removed by the resin. However, recovery of the dye from the resin column by backwashing with selected solvents did leave some dye remaining on the column. This was evident from the slight color change in the resin that could be observed after backwashing. Alternative methods for removal of the tightly bound dye from the resin were, therefore, investigated.

In previous work the resin column was inverted and backwashed with selected solvents to remove the disperse and acid dyes.

An improved technique for removal of a mixture of dyes adsorbed on macroreticular resins based on a soxhlet extraction process was attempted. The dried resin collected in the extraction thimble was placed in a soxhlet unit and extracted using selected solvents. The resin was first extracted for four hours using benzene to remove disperse dyes. The resin was removed, dried, and returned to the soxhlet unit again. The acid dyes were removed by extraction with methanol and then with pyridine-THF-1% NH_4OH (40:40:20). In this separation system, the recovery efficiency was excellent for disperse dyes but was poor for acid dyes. Other techniques were studied, therefore, for removal of acid dyes. Extractions using pure pyridine and immersion of resins in solvent mixtures of THF-1% NH_4OH and MeOH-1% NH_4OH prior to extraction were tried. None of these procedures gave good removal of acid dyes. Finally, an improved technique for the analysis of acid dyes was developed. After removal of the disperse dyes with benzene, a mixed solvent containing 90-ml of pyridine - 2% NH_4OH (50:50) was added to the extraction thimble. This system was allowed to stand for one hour. The acid dyes were then removed from the resin by extraction with boiling pyridine. The dyes removed by benzene (disperse dyes) and pyridine (acid dyes) were further concentrated by evaporation of solvent in a rotary evaporator. The solid dyes obtained from vaporization were prepared for analysis by taking them up in a DMF 1% - benzene 99% solution for disperse dyes, and in a DMF 1% - methanol 99% solution for acid dyes. Twenty five mls of solution were prepared for standard samples giving a concentration factor of 40. The dyes

were separated and quantitated using the high pressure liquid chromatograph described previously.

To determine recovery efficiency 1 liter (water 900-ml - DMF 100 ml) of 1 ppm concentrations of each of fifteen dyes was analyzed as described above. The results are shown in Table 17. These data show that the recoveries are 100% for Disperse Yellow 3, Disperse Red 55, Disperse Red 60, Acid Red 337, and Acid Orange 128; above 95% for Disperse Blue 7, Acid Yellow 135, Acid Yellow 151, Acid Red 151, and Acid Blue 25; between 90% to 95% for Disperse Yellow 23, Disperse Yellow 54, and Acid Blue 40; and about 82% for Disperse Blue 120 and Acid Yellow 19. The recoveries are considerably better than those achieved in previous work as can be seen by comparing Table 17 and Table 18. Further details on this work are available in reference 26.

C. Extension of the Analytical System to Direct Dyes

Direct dyes are used extensively in dyeing both textiles and paper products. Discussions with manufacturers of direct dyes suggested that the following direct dyes are used in very large volume:

Direct Yellow 105

Direct Yellow 106

Direct Red 80

Direct Red 81

Direct Blue 98

Direct Blue 218

These six dyes were selected for initial studies to develop an analytical system for direct dyes. Structures of four of these dyes have been published

Table 17. Recovery for Disperse and Acid Dyes Analyzed by the Improved Analytical System*

Disperse Dyes	Recovery (%)	Acid Dyes	Recovery (%)
Disperse Yellow 3	100	Acid Yellow 19	82
Disperse Yellow 23	90	Acid Yellow 135	97
Disperse Yellow 54	91	Acid Yellow 151	98
Disperse Red 55	100	Acid Red 151	98
Disperse Red 60	100	Acid Red 337	100
Disperse Blue 7	98	Acid Orange 128	100
Disperse Blue 120	83	Acid Blue 25	95
		Acid Blue 40	92

* Disperse dyes were extracted with benzene, and acid dyes were immersed in pyridine - 2% NH_4OH (50:50) for one hour and then extracted with pure pyridine.

Table 18. Recovery Data of Previous Work*

Disperse Dyes	Recovery (%)	Acid Dyes	Recovery (%)
Disperse Yellow 3	98	Acid Yellow 19	70
Disperse Yellow 23	77	Acid Yellow 135	100
Disperse Yellow 54	77	Acid Yellow 151	75
Disperse Red 55	95	Acid Red 151	97
Disperse Red 60	89	Acid Red 337	75
Disperse Blue 7	73	Acid Orange 128	76
Disperse Blue 120	83	Acid Blue 25	80
		Acid Blue 40	84

* Disperse dyes were eluted with benzene and acid dyes were eluted with methanol and then with pyridine - THF - 1% NH_4OH (40:40:20).

and are shown in Appendix B [27]. Structures of Direct Yellow 105 and Direct Yellow 106 have not been published although they are listed as stilbene derivatives.

Direct dyes contain large quantities of salts in addition to the dye. A purification procedure was required, therefore, to obtain samples for standard preparation. The technique used for purification [28] involved, first, dissolving the dye in DMF and filtering. The dye is soluble in DMF but the various inorganic salts present are not soluble. The dye is then recovered from DMF by addition of acetone to precipitate the dye. The precipitated dye is filtered, washed with acetone, and dried. This procedure was carried out twice to obtain purified dyes for preparation of standards.

Adsorption spectra of the six direct dyes selected for study are shown in Figures 11 and 12. A wavelength of 420 nm was selected for analysis for the yellow dyes, 520 nm for red dyes and 600 nm for blue dyes. It is clear from the spectra in Figures 11 and 12 that some absorbance from the red dyes will occur at 420 nm. Therefore, possible interference of the red dyes with analysis of the yellow dyes was expected. Similar problems should not be encountered in analysis for the direct red and direct blue dyes.

The structures of acid and direct dyes are similar in that both classes of dyes contain one or more ionic sodium sulphonate groups. It was expected, therefore, that the paired ion chromatograph (PIC) technique used to separate acid dyes could also be used for direct dyes. Initial experiments conducted by injecting solutions of direct dyes in 99% methanol-17% DMF in the liquid chromatograph (equipped with a C-18 bonded column) and eluting with a

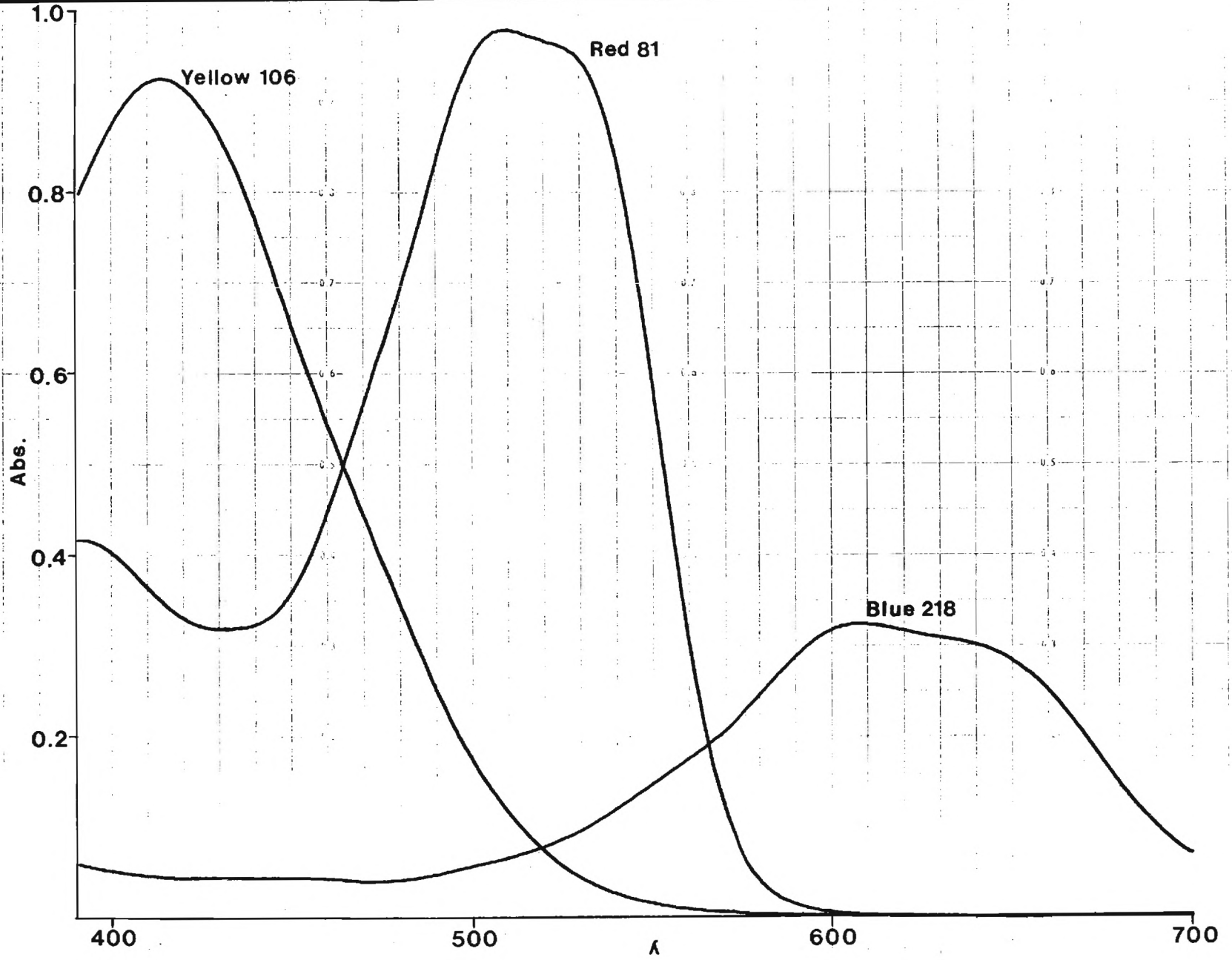

Fig. 11. Spectrophotometric Curves of Direct Yellow 106, Direct Red 81 and Direct Blue 218

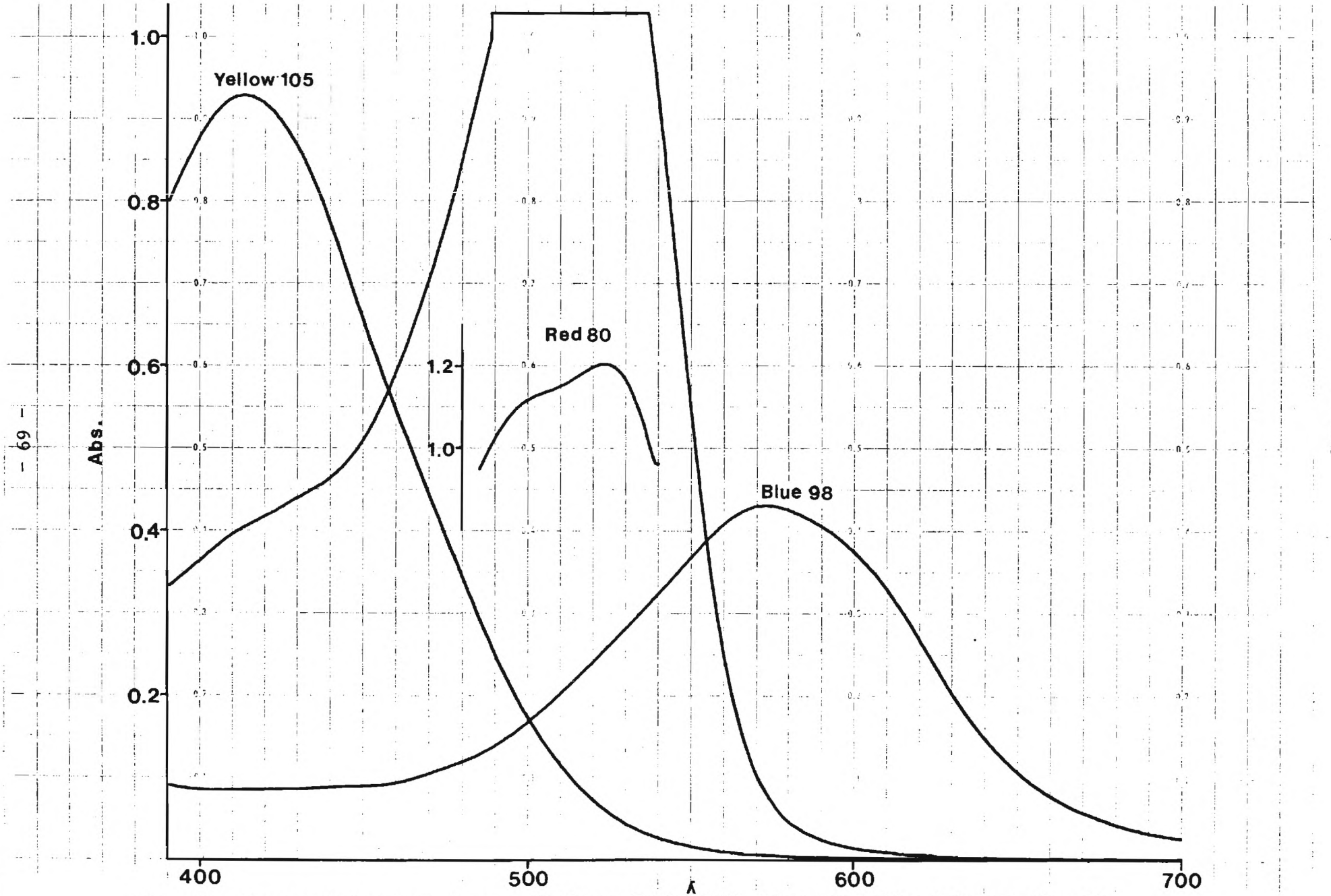

Fig. 12. Spectrophotometric Curves of Direct Yellow 105, Direct Red 80 and Direct Blue 98

methanol water solvent mixture containing tetrabutylammonium phosphate confirmed this expectation. A chromatogram of a dye mixture containing 5 ppm each of Direct Yellow 106, Direct Yellow 105, Direct Red 80 and Direct Red 81 is shown in Figure 13. This chromatogram was obtained by a linear gradient elution beginning at 50/50 methanol/water and concluding at 85/15 methanol/water. The gradient time was 30 minutes at a total flow rate of 1 ml per minute. The detector was set at 420 nm. Both the direct yellow dyes are clearly separated and could be readily quantitated. It is interesting to note that Direct Yellow 105 gives two very distinct peaks in the chromatogram. Similar multiple peaks were found for most of the direct dyes.

A similar chromatogram of Direct Red 80 and Direct Red 81 is shown in Figure 14. The same gradient as above was run over a 10 minute period with the detector set at 520 nm. The two peaks from Direct Red 80 are clearly separated from Direct Red 81 under these conditions. It should be noted that the two peaks marked with X's in the chromatogram are artifacts due to a malfunction of the injector during this run.

Studies on Direct Blue 98 and Direct Blue 218 have shown that peaks from the dyes are separated very well with a 10 minute gradient from 50/50, methanol/water, to 85/15, methanol/water.

Thus, results of the liquid chromatography studies show that paired ion chromatography is a very effective technique for separating and quantitating direct dyes.

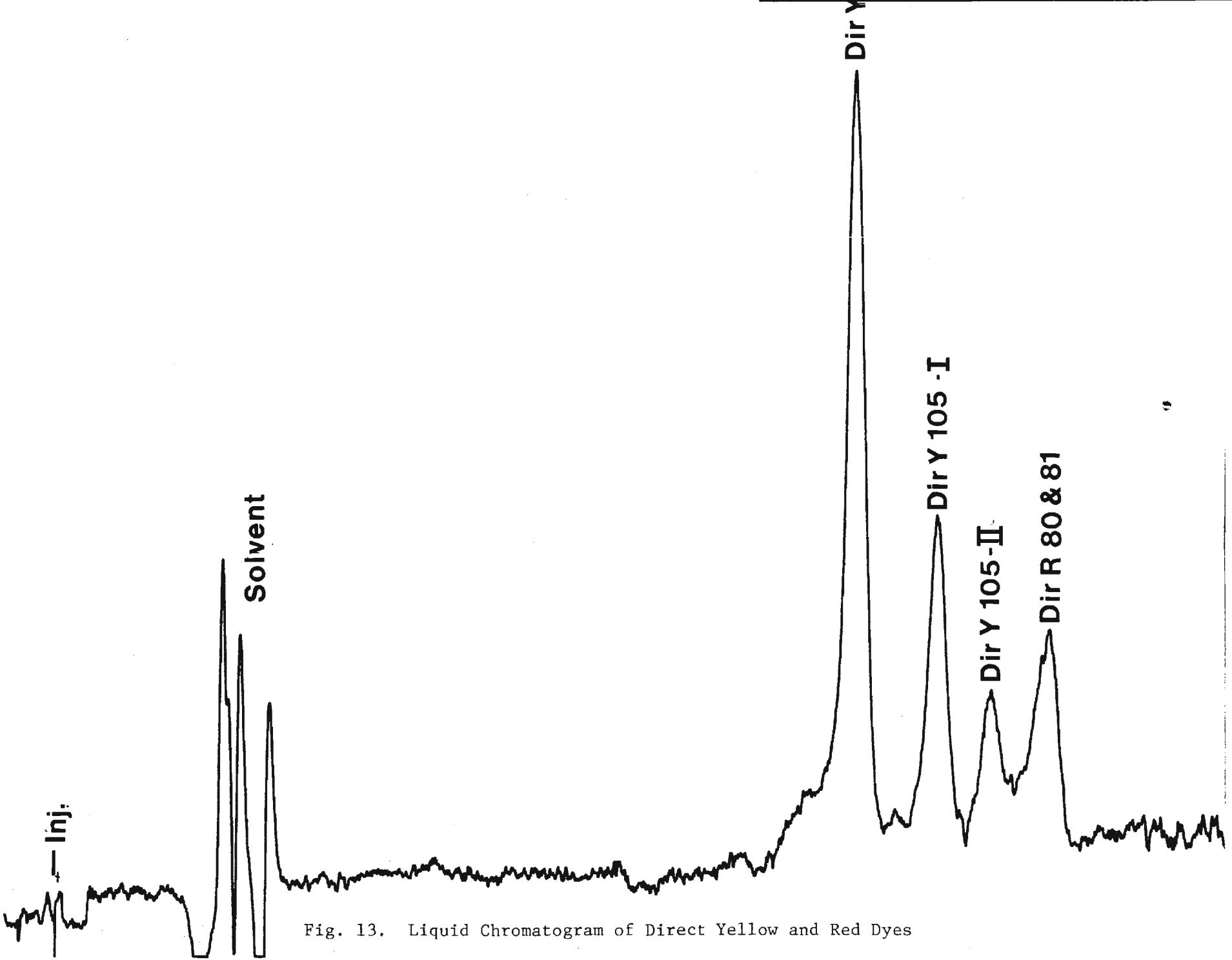

Fig. 13. Liquid Chromatogram of Direct Yellow and Red Dyes

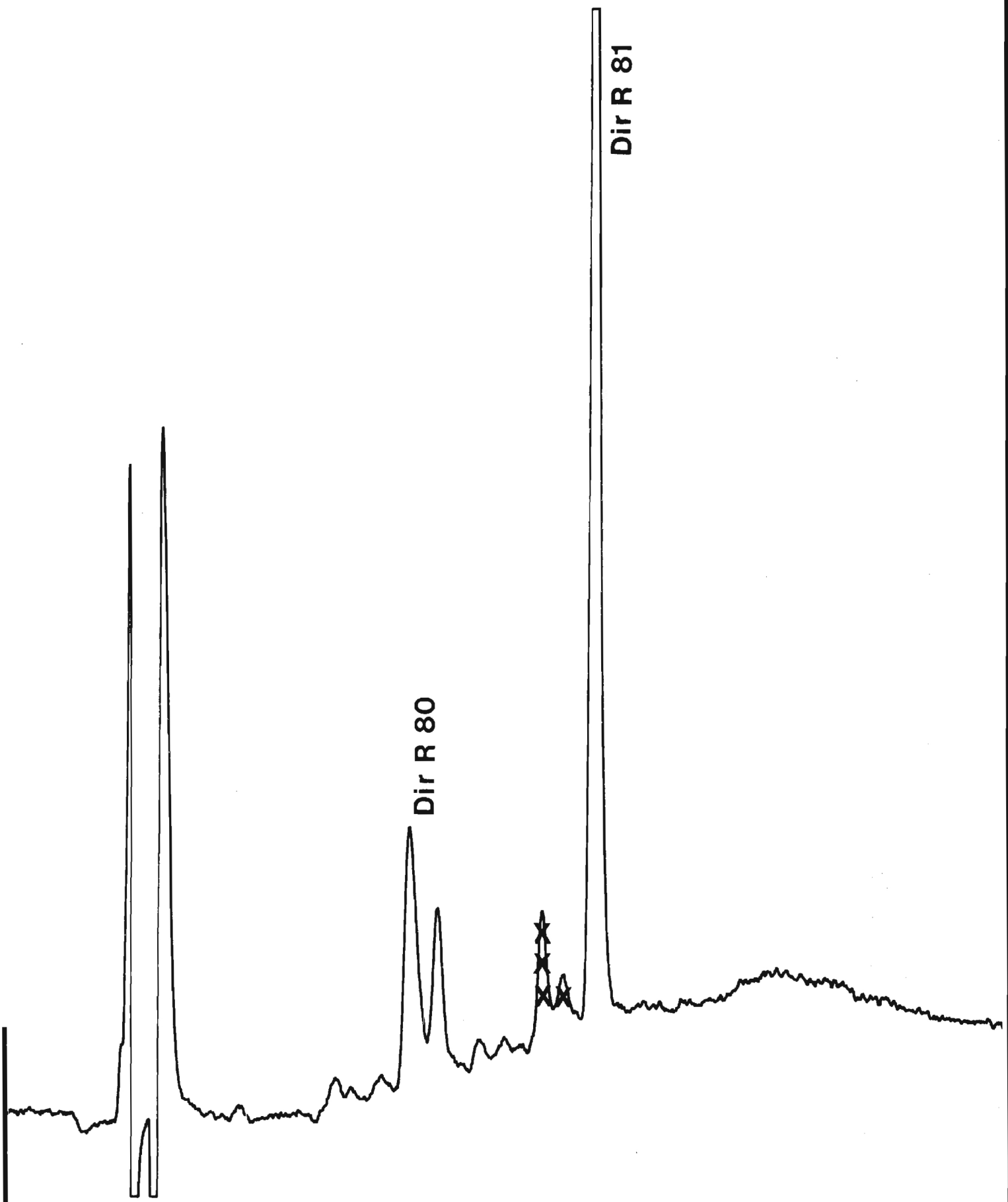

Fig. 14. Liquid Chromatogram of Direct Red Dyes

Preliminary experiments were also carried out to investgiate the removal and concentration of direct dyes from wastewater. These experiments indicate that direct dyes can be removed from water by XAD-2 macroreticular resins. They are also removed from the resin by Sohxlet extraction with methanol. Thus, concentration procedures similar to those used for acid dyes should be applicable to direct dyes. Limitations in time and funds did not permit a complete study of the concentration phase.

Since acid dyes and direct dyes will be removed from the XAD resin columns by the same solvents, some experiments were carried out to determine if the acid and direct dyes could be separated and quantitated on the liquid chromatograph. A mixture of Direct Yellow 105, Direct Yellow 106, Direct Red 80, Direct Red 81, Acid Yellow 19, Acid Yellow 151 and Acid Yellow 135 were injected into the Chromatograph and a gradient run beginning at 55/45, and concluding at 85/15, methanol/water over a 30 minute period gave the chromatograph shown in Figure 15. Under these conditions Direct Yellow 106 begins to split into two components. The only overlap is the Acid Yellow 19 peak with one of the Direct Yellow 105 peaks. By determining the concentration of the Direct Yellow 105 from the second peak and correcting the area of the overlap peak for the Direct Yellow 105 peak I, all 5 acid and direct yellow dyes can be quantitated.

In conclusion, the preliminary results suggest that the resin concentration-liquid chromatography system can be readily applied to analysis for direct dyes in wastewater. Further development of the system should make quantitative analysis of dyes in cotton and cotton polyester blend dyeing and in paper coloration wastewater a reality.

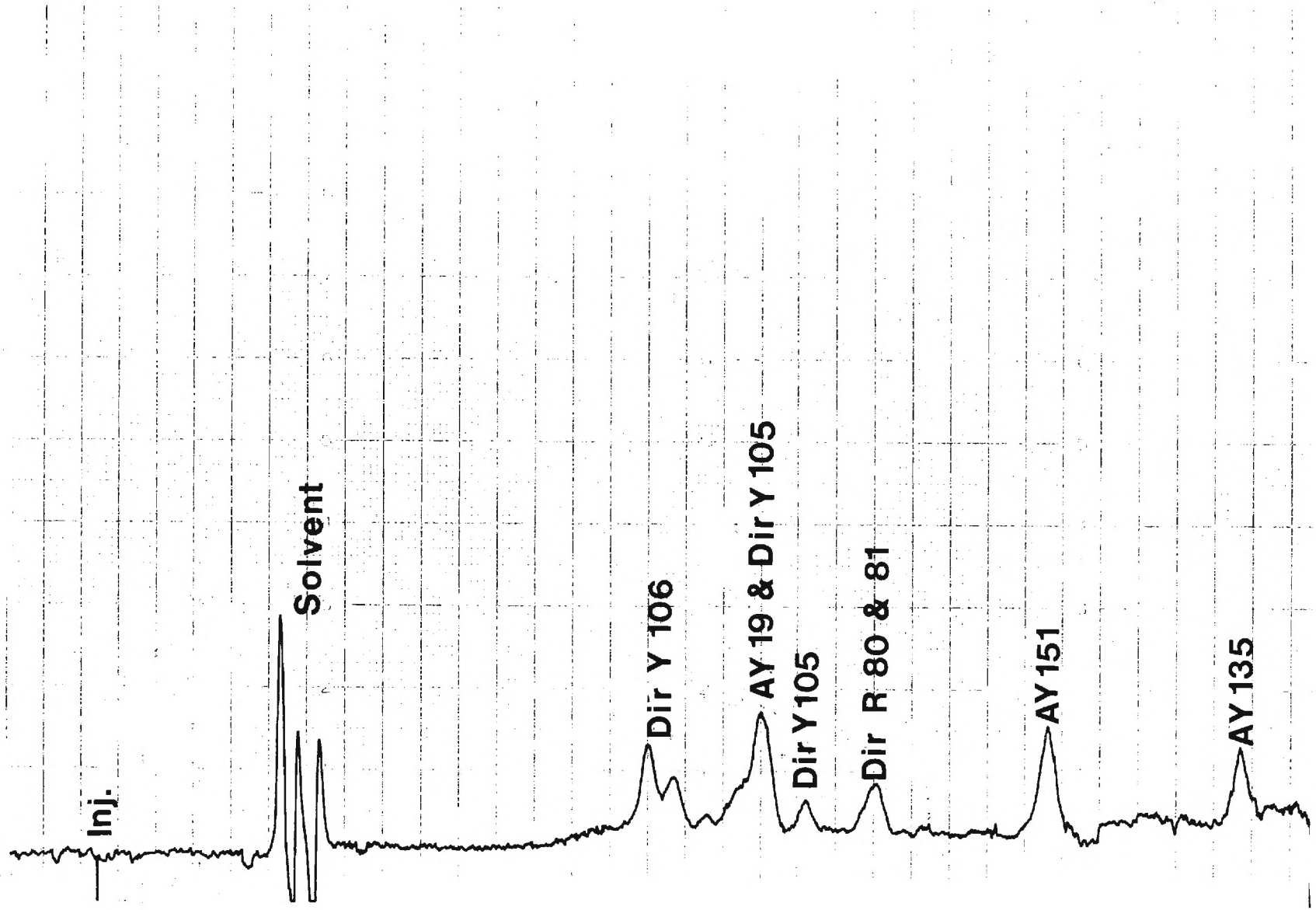

Fig. 15. Liquid Chromatograph of a Mixture of Direct Yellow, Direct Red and Acid Yellow Dyes

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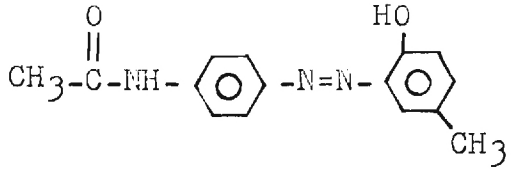
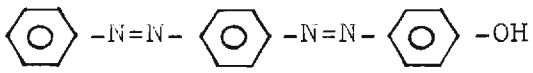
Appendix A

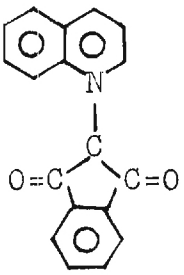
Disperse Yellow 3



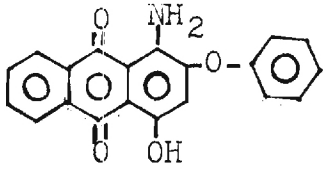
Disperse Yellow 23



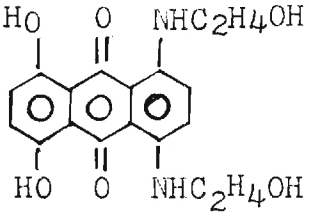
Disperse Yellow 54



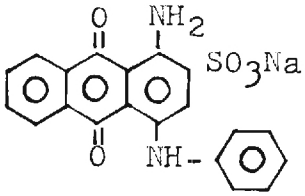
Disperse Red 60



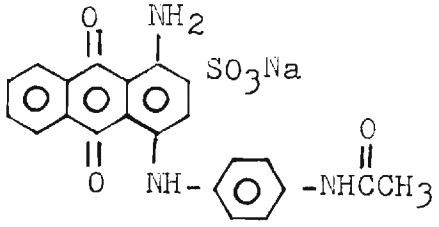
Disperse Blue 7



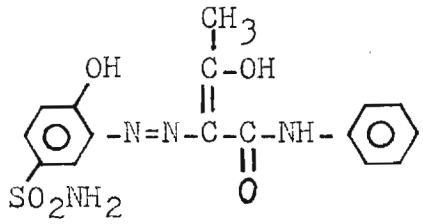
Acid Blue 25



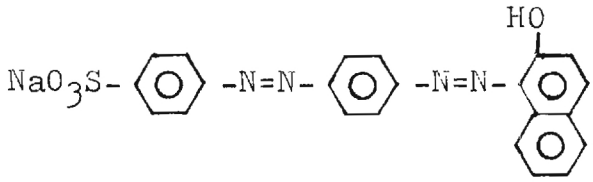
Acid Blue 40



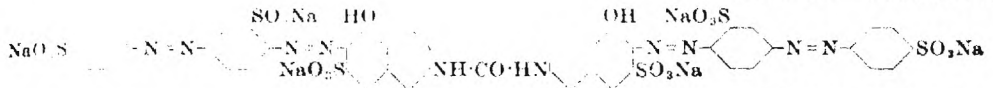
Acid Yellow 151



Acid Red 151



35780 **C.I. Direct Red 80** (*Bright bluish pink* → *Bright bluish red*)



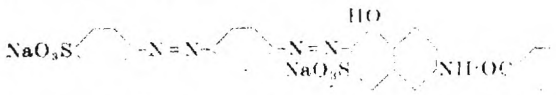
(*a*) *b*-Amino-3,4′-azodibenzenesulfonic acid → *N*-Acetyl J acid; *then hydrolyse the acetamido group and phosgenate, or*

(*b*) 6-Amino-3,4′-azodibenzenesulfonic acid (2 mol.) ⇉ 6,6′-Ureylenebis-1-naphthol-3-sulfonic acid

Discoverer — J. P. Penny 1922
National Aniline, *USP* 1509442
FIAT 764 — Siriusrot F3B

Soluble in water (bluish red to magenta)
Very slightly soluble in ethanol and Cellosolve
Insoluble in other organic solvents
H_2SO_4 conc. — blue; on dilution — bluish red to violet
HNO_3 conc. — blue
Aqueous solution + HCl conc. — violet ppt;
+ NaOH conc. — reddish violet

28160 **C.I. Direct Red 81** (*Bright red*)



p-(*p*-Aminophenylazo)benzenesulfonic acid → *N*-Benzoyl J acid

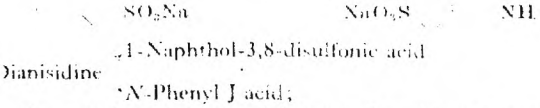
Aqueous solution + HCl conc. — yellowish olive brown ppt;
+ NaOH conc. — violet ppt.

Discoverers — L. Hesse, O. Günther and A. Zart 1909
Bayer Co., *BP* 476809; *USP* 931423-4; *FP* 402126; *GP* as F25375 (*Fr.* 10, 896)
BIOS 1548, 160
FIAT 764 — Siriusrot 4B
Wanner, *Z. angew. Chem.* **38** (1925), 513

Soluble in water (magenta red)
Slightly soluble in ethanol
Insoluble in other organic solvents
H_2SO_4 conc. — deep blue; on dilution — pale orange brown ppt
HNO_3 conc. — bright blue solution, turns reddish brown

23155 **C.I. Direct Blue 98** (*Blue*)

Bis Copper complex, derived from



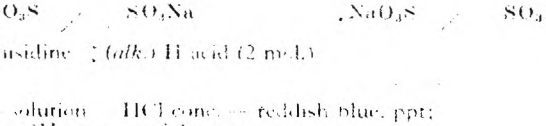
1-Naphthol-3,8-disulfonic acid
+ Dianisidine
+ *N*-Phenyl J acid;

then make an intimate mixture of the paste dye with an aqueous solution of copper sulfate and sodium acetate by mixing for 1½ days and then dry under vacuum at 120–125 C. The two methoxyl groups are replaced by hydroxyl groups during the process

Discoverers — R. Stüsser and R. Wiedemann 1929
I.G., *BP* 352956; *USP* 1889732; *FP* 712993; *GP* as (*Fr.* 18, 1035)
BIOS 1548, 132
FIAT 764 — Siriuslichtblau FBGL

Soluble in water (reddish blue)
Very slightly soluble in ethanol
H_2SO_4 conc. — greenish blue; on dilution — dullish violet
Aqueous solution + HCl conc. — violet ppt;
+ NaOH conc. — reddish blue ppt.

24400 **C.I. Direct Blue 15** (*Blue*) (Blue 218 with Cu)



Dianisidine → (*talk*) H acid (2 mol.)

Aqueous solution + HCl conc. — reddish blue ppt;
+ NaOH conc. — violet ppt.

Discoverers — J. Baumann, M. Ulrich and M. Hoffmann 1890
Cassella Co., *BP* 17429/1; *USP* 464135, 498874, 501500; *FP* 201770; *GP* 74593 (*Fr.* 3, 684)
BIOS 1548, 175
FIAT 764 — Benzorenblau

Soluble in water (reddish blue)
Insoluble in organic solvents
H_2SO_4 conc. — bluish green; on dilution — reddish brn.
HNO_3 conc. — reddish grey solution

APPENDIX C

Analytical Procedure for Analysis of Dyes in Wastewater

Scope: This method is applicable to the determination of 15 acid and disperse dyes (Acid Yellow 19, Acid Yellow 135, Acid Yellow 151, Acid Orange 128, Acid Red 151, Acid Red 337, Acid Blue 25, Acid Blue 40, Disperse Yellow 3, Disperse Yellow 23, Disperse Yellow 54, Disperse Red 55, Disperse Red 60, Disperse Blue 7, Disperse Blue 120) in wastewater.

Apparatus: Chromatography Columns (9 mm x 500 mm) equipped with demountable stopcocks and reservoirs. Rotary vacuum evaporator. High-pressure liquid chromatograph equipped with variable wavelength UV-visible detector and solvent gradient capability. Soxhlet extractor (large).

Chemicals: Liquid Chromatography Grade Dimethylformamide
Liquid Chromatography Grade Cyclohexane
Liquid Chromatography Grade Tetrahydrofuran
Liquid Chromatography Grade Methanol
Liquid Chromatography Grade Benzene
High Purity Distilled Water
PIC Reagent A (Tetrabutyl ammonium phosphate)--Waters Associates
Dye Samples for standard preparation

Purified Dye Samples: Disperse Dyes--Place 50 grams of disperse dye in a glass extraction thimble (course fritted disk). Extract in a Soxhlet extraction unit until extract is clear. Evaporate extract in a rotary vacuum evaporator until dry. Repeat the extraction on the recovered dye. Place the reserved pure dye from the second extraction in a tightly closed container and place in a dessicator.

Acid Dyes--Dissolve 50 grams of acid dye in 300 ml of dimethylformamide. Filter and retain the filtrate. Precipitate the dye from the diemethylformamide by the addition of 300 ml of acetone. Recover the dye by filtration. Repeat the purification. Place the pure dye recovered from the last filtration in a tightly closed container and place in a dessicator.

Standard Solutions: Weigh 1.00000 gram of purified disperse dye and transfer to a 1 liter volumetric flask. Add 10 ml of dimethylformamide (LC grade) and fill to calibration mark with benzene (LC grade) for a 1 gram per liter standard stock solution. For standard acid dye solutions, weigh 1.00000 gram of purified acid dye and transfer to a 1 liter volumetric flask. Add 10 ml of dimethylformamide (LC grade) and fill to calibration mark with methanol (LC grade). Prepare 5, 10 and 20 ppm solutions of dyes by pipetting the appropriate quantity of stock solution into a 100 ml volumetric flask and diluting to the calibration mark with 1% DMF/99% benzene (LC grade) for disperse dyes or 1% DMF/99% methanol (LC grade) for acid dyes.

Wastewater Samples: Wastewater samples should be collected in clean glass bottles and kept at 0°C until concentrated.

Resin Column Preparation: Place approximately 50 cc of Amberlite XAD-2 macroreticular r-sin (Rohm and Haas Company) in a glass Soxhlet extraction thimble. Extract with 250 ml of methanol for 2 hours. Discard the methanol and extract with benzene for 2 hours. Discard the benzene and fill the extraction thimble with a 50:50 pyridine:2% ammonium hydroxide solvent mixture. Allow to stand for one hour then extract for 2 hours with pyridine. Discard the pyridine/ammonium hydroxide solution and dry the purified resin in a warm (75°C) oven. Slurry the purified resin in 100 ml of methanol. Pour the slurry into a prepared chromatography column allowing the methanol to drain through the stopcock. Collect approximately 30 ml of resin in the column. Downflow wash the resin with 200 ml of water followed by an upflow wash of 40 ml of water to reclassify the column. Store the column under distilled water until ready for use.

Dye Concentration: Take 1800 ml of the wastewater sample and add 200 ml of DMF. Divide the sample in two approximately equal portions and pass the solution through two prepared XAD-2 resin columns at 4 bed volumes (120 ml) per hour. Rinse the column with 40 ml of distilled water. Drain as much water from the column as possible then transfer the resin from both columns into a single large extraction thimble. Dry the resin-containing dye in a warm (75°C) oven overnight. Place the extraction thimble in a soxhlet extractor and extract with benzene until the extract is clear (approximately 4 hours). Place the extract in a rotary evaporator and evaporate to dryness. Take the extracted dye up in 10 ml of a 1% DMF/ 99% benzene solvent mixture. After extraction of the resin with benzene place the resin and thimble in the drying oven to remove residual benzene. Return the dry resin to the Soxhlet extractor and fill the thimble with a 50:50, pyridine:2% ammonium hydroxide solvent mixture. Allow to stand for 1 hour and then extract with pyridine until the extract is clear (approximately 4 hours). Place the extract in the rotary evaporator and evaporate to dryness. Take the residue up in 10 ml of a 1% DMF/99% methanol solvent mixture.

Analysis for Disperse Dyes: Place a 25 cm column with cyanoethyl groups bonded to a silica substrate (Partisil 10-PAC from Whatman or equivalent) in the liquid chromatograph. All analyses are run with a 1 ml/minute solvent flow rate and with a 20 microliter sample size.

Red 55--Equilibrate the column by flowing 35/65 mixture of tetrahydrofuran/cyclohexane through the column for 15 minutes. Monitor the effluent at 520 nm. Inject samples of the 5, 10 and 20 ppm standard solutions of Disperse Red 55 sequentially into the chromatograph. The dye peak appears just after the solvent front (see Figure 3). Prepare a plot of area under the curve versus concentration. Inject a sample of the concentrated disperse dye mixture. Determine the area of the peak from Disperse Red 55. Determine the concentration of Disperse Red 55 from the calibration curve. Strip other dyes from the column by passing 100% tetrahydrofuran through the column for 15 minutes.

Red 60--Equilibrate the column by flowing a 80/20 tetrahydrofuran/cyclohexane solution through the column for 15 minutes. Monitor the effluent at 520 nm. Inject samples of the 5, 10 and 20 ppm standard solution of Disperse Red 60 sequentially into the chromatograph. The dye peak will appear just after the solvent front. Prepare a plot of area under the peak versus concentration. Inject a sample of the concentrated disperse dye mixture. Determine the area under the peak from Disperse Red 60. Determine the concentration of Disperse Red 60 from the calibration curve. Strip other dyes from the column by passing 100% THF through the column for 15 minutes.

Blue 120--Equilibrate the column by flowing a 45/55 tetrahydrofuran/cyclohexane mixture through the column for 15 minutes. Monitor the effluent at 620 nm. Inject samples of the 5, 10 and 20 ppm standard solution of Disperse Blue 120 sequentially into the chromatograph. The dye peak will appear just after the solvent front. Prepare a plot of area under the peak versus concentration. Inject a sample of the concentrated disperse dye mixture. Determine the area under the peak from Disperse Blue 120. Determine the concentration of Disperse Blue 120 from the calibration curve. Strip other dyes from the column by passing 100% THF through the column for 15 minutes.

Blue 7--Equilbrate the column by passing 100% THF through the column for 15 minutes. Monitor the effluent at 620 nm. Inject samples of the 5, 10 and 20 ppm standard solutions of Disperse Blue 7 sequentially into the chromatograph. Several peaks will appear with two principal peaks at approximately 2 and 4 minutes retention time (see Figure 2). Determine the area of either of the two major peaks and plot area under the peak versus concentration. Inject a sample of the concentrated disperse dye mixture. Determine the area under the selected peak and obtain the concentration of Disperse Blue 7 from the calibration curve.

Yellow Dyes--The three yellow disperse dyes can be determined from a single sample injection. The column is equilibrated by pumping a 25/75 mixture of tetrahydrofuran/cyclohexane through the column for 15 minutes. The effluent is monitored at 420 nm. A 20 microliter sample of 20 ppm of each of the yellow dyes is injected and a solvent gradient varying linearly from 25/75 to 100/0 tetrahydrofuran/cyclohexane is run over 15 minutes. Disperse Yellow 54 elutes first followed by Disperse Yellow 23 with Disperse Yellow 3 eluting last (see Figure 1). Reset the gradient controller to 25/75 tetrahydrofuran/cyclohexane. Repeat the calibration procedure by injecting standard solution containing 10 ppm of each disperse yellow dye and 5 ppm of each disperse yellow dye. Plot areas under the peaks versus concentration for each of the yellow disperse dyes. Inject a 20 microliter sample of the concentrated disperse dye mixture and elute with the solvent gradient. Determine the areas under the peaks eluting at the same times as the santdards and calculate the concentration from the areas using the calibration curves.

Analysis for Acid Dyes: Place a 25 cm 5 micron silica with C-18 hydrocarbon bonded to the surface column (e.g., Spherisorb ODS, Laboratory Data Control) in the liquid chromatograph. Prepare the elution solvents by dissolving 1 vial of buffered tetrabutylammonium phosphate (PIC Reagent A, Waters Associates) in methanol (LC grade) and 1 vial in high purity distilled water. Filter the solvents to remove any particulates from the PIC A reagent. Prepare a 60/40, methanol/water, solvent mixture and an 85/15, methanol/water, mixture. The 60/40 mixture is used as solvent A in the gradient system and the 85/15 mixture as solvent B. Filter both solvents A and B and heat the filtrate for 1 minute at the boil under reflux to degress the solvents. A flowrate of 1 ml per minute, a solvent gradient of 0% A to 100% B over a 10 minute period is employed in all acid dye analyses. A flowrate of 1 ml per minute is used.

Acid Blue Dyes--Set the detector at 615 nm. Inject a solvent blank (20 microliters of a 1% DMF/99% methanol solvent mixture) and run the elution gradient. This run will serve for background calibration. Reset the gradient programmer to 0% A. Inject a 20 microliter sample of a 20 ppm mixture of Acid Blue 40 and Acid Blue 25. Two major peaks will be observed with the Acid Blue 40 peak appearing first (see Figure 6). Run a 10 ppm mixture and a 5 ppm mixture of each of the Acid Blue dyes in a similar manner. Prepare a plot of peak area versus concentration for each of the Acid Blue dyes. Inject a 20 microliter sample of the dye concentrate from the wastewater and elute in the same manner as the standards. Determine the area under the peaks eluting at the same time as Acid Blue 40 and Acid Blue 25 and determine their concentration from the calibration curves.

Acid Red and Orange Dyes--Set the detector at 520 nm. Inject a solvent blank (20 microliters of a 1% DMF/99% methanol solvent mixture) and run the elution gradient for background calibration. Reset the gradient programmer to 0% A. Run a 20 ppm, 10 ppm and 5 ppm standard mixture of Acid Red 337, Acid Orange 128 and Acid Red 151, sequentially. The Acid Red 337 peak appears first, the Acid Orange 128 second and the Acid Red 151 last (see Figure 5). Prepare calibration curves with peak area plotted against concentration for each of these dyes. Inject a 20 microliter sample of the dye concentrate from the wastewater and elute in the same manner as the standards. Determine the areas under the peaks eluting at the same time as peaks in the chromatograms of the standards and determine the concentrations from the calibration curves.

Acid Yellow Dyes--Set the detector at 420 nm. Inject a solvent blank (20 microliters of a 1% DMF/99% methanol solvent mixture) and run the elution gradient for background calibration. Reset the gradient program to 0% A. Run a 20 ppm, 10 ppm and 5 ppm standard mixture of Acid Yellow 19, Acid Yellow 151 and Acid Yellow 135, sequentially. If Acid Orange 128 was present in the wastewater sample (see above) run 20 ppm, 10 ppm and 5 ppm standard samples of Acid Orange 128. The Acid Yellow 19 peak appears first, the Acid Yellow 151 peak next and the Acid Yellow 135 peak appears last (see Figure 4). The Acid Orange 128 peak elutes at the same retention time as Acid Yellow 151. Prepare calibration curves of peak area versus concentration for the Acid Yellow and Acid Orange dyes. Inject a 20 microliter sample of the dye concentrate from the wastewater and elute in the same manner as the stan-

dard dye solutions. Determine the areas under the peaks eluting at the same retention time as peaks in the chromatograms of the standards. Calculate the concentrations of Acid Yellow 19 and Acid Yellow 135 from the calibration curves. Using the Acid Orange 128 calibration curve calculate the area of the peak expected at 420 nm from the concentration of Acid Orange 128 found previously. Subtract this area from the second peak (combined Acid Orange 128 and Acid Yellow 158). Determine the concentration of Acid Yellow 151 from the remainder using the appropriate calibration curve.

Sensitivity: All dyes except Disperse Blue 7 and Disperse Blue 120 can be detected at 1 part-per-billion in wastewater. Acid Blue 7 can be detected at 10 parts-per-billion and Acid Blue 120 at 25 parts-per-billion.

Other Applications: The analytical system can be used for solid (mud) samples by extracting the dry mud in exactly the manner described for the soxhlet extraction of the resin in the dye concentration phase. A total of 1,000 grams of dry mud should be extracted for subsequent analysis.